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1

General Principles and Processes of Isolation of Elements

OVERVIEW

- The most abundant element in the earth's crust is oxygen.
- The most abundant metal in the earth's crust is aluminium.
- The most abundant transition metal in the earth's crust is iron.
- The earth's crust is the biggest source of metals. Metals occurs in nature in (i) native and (ii) combined states.
- Natural substances in which metals or their compounds occur in earth are called **minerals**. Minerals from which metals can be conveniently and economically extracted are called **ores**.
- All ores are minerals, but all minerals are not ores.
- Ores may be classified as
 - Native ores
 - Combined ores – oxides, halides, sulphides etc.
- The process of extraction of the metal (in the pure form) from its ore is called **metallurgy**.
- Various steps involved in the extraction of a metal from its ores are as follows:
 - Grinding and pulverising the ore.
 - Concentration of the ore or ore-dressing.
 - Reduction of concentrated ore to the crude metal.
 - Refining of the crude metal.
- The unwanted impurities, e.g. clay, associated with the ore are known as **gangue** or **matrix**.
- Concentration of the ore or ore dressing is the process of removal of gangue from the ore.
- Depending on the nature of the ore, ore-dressing is done by:
 - Hand picking
 - Hydraulic washing or gravity separation method:** Native ores of Au, Ag, etc. and oxide ores of iron and tin are concentrated by this process.
 - Electromagnetic separation method:** This method is used when either the impurities or ore are magnetic in nature. For example,
 - Chromite ore (magnetic) is separated from non-magnetic siliceous impurities.
 - Wolframite ore (magnetic) (FeWO_4) is separated from non-magnetic cassiterite ore (SnO_2).
- Froth flotation process:** Used for concentration of sulphide ores. The process is based on preferential wetting of ore particles by oil and gangue particles by water.
- Leaching:** Involves treating the ore with a suitable reagent to make it soluble while impurities remain insoluble. For example, native ores of Ag and Au are treated with NaCN in the presence of oxygen.
- Reduction of the concentrated ore to the crude metal involves:
 - Conversion of the ore into metallic oxide by either calcination or roasting.
 - Reduction of metallic oxide to free metal by:
 - Smelting or pyrometallurgy:** It is applicable mainly for the extraction of less electropositive metals such as Fe, Zn, Sn, Pb etc. by using C, CO, and Al as reducing agents.
 - Reduction of Al:** Goldschmidt aluminothermic process is used in case of those metals that have very high melting points and are to be extracted from their oxides.
 - Self or auto-reduction process:** The sulphide ores of less electropositive metals are heated in air so as to convert a part of the ore into oxide or sulphate, which further reacts with remaining sulphide ore to give metal and SO_2 .
 - Electrolytic reduction:** Highly electropositive metals such as alkali metals are extracted by the electrolysis of hydroxides, chlorides or oxides in the fused state.
 - Hydrometallurgy.
- Basic concepts of thermodynamics is quite useful in selecting a suitable reducing agent for a particular oxide. In the oxidation reduction reaction, $\Delta_f G^\ominus$ should be negative at appropriate temperatures.

$$\Delta_f G^\ominus = \Delta_f H^\ominus - T\Delta_f S^\ominus$$
 The concept is graphically displayed by $-\Delta_f G^\ominus$ vs T (in K) plots, i.e. Ellingham diagram.
- Purification or refining:** Process of purifying impure metals is called refining. It can be done by:

- a. **Physical methods:** Liquation, distillation, zone refining, vacuum arc furnace refining etc.
- b. **Chemical methods:** Pyrometallurgical oxidation, electrolytic refining, vapour phase refining—Mond's or Van Arkel method, chromatographic separation, ion exchange methods, solvent extraction methods, Parting's process etc.

16. Furnaces:

- a. **Reverberatory furnace:** Used for roasting, smelting etc.
- b. **Muffle furnace:** Used when high temperature is required.
- c. **Blast furnace:** Temperature at bottom is 1500°C and at the top is $200\text{--}300^{\circ}\text{C}$.
- d. **Electric furnace:**
 - i. **Arc furnace:** Temperature ranges from 3000 to 3500°C .
 - ii. **Resistance furnace:** Temperature ranges from 3000 to 4000°C .
 - iii. **Induction furnace:** Temperature is 3000°C .

- 17. Many of the metals/non-metals are found in traces in living organisms, for example
 - a. Iron is found in haemoglobin.
 - b. Sodium in blood.
 - c. Magnesium in chlorophyll.
 - d. Mn, Fe and Cu in chloroplast.
 - e. Zn in eyes of cows and cats.
 - f. Cr in prawns.
 - g. Ca in bones.
 - h. Vanadium in cucumbers.
 - i. Iodine in sea weeds.
- 18. Active metals like Li, Na, K, Ca, Mg, Sr, Ba etc. are obtained by the electrolysis of their fused chlorides, oxides or hydroxides.
- 19. Noble metals like Au, Ag etc. are obtained by cyanide or amalgamation process.
- 20. Heavy metals like Cu, Zn, Fe, Pb etc. are obtained by roasting and smelting process.
- 21. Thomas slag is $\text{Ca}_3(\text{PO}_4)_2$.
- 22. A mixture of iron oxide (Fe_2O_3) and Al powder in the ratio $3 : 1$ is called **thermite mixture**. A mixture of Mg powder and BaO_2 is called **ignition powder**.

1.1 ABUNDANCE OF ELEMENTS IN THE EARTH'S CRUST

Earth's crust is made up of light elements, such as oxygen, silicon and aluminium. Oceanic crust is mostly basalt (which also contains magnesium and iron). Continental crust is composed of two main types of igneous rocks.

1. Light rocks, i.e. granite and related types (containing 70% SiO_2 together with Al_2O_3).
2. Heavy rocks, i.e. basalt (containing 40–50% SiO_2 together with MgO).

Al is the second most abundant element in light rocks, and Mg is the second most available element in heavy rocks.

The relative abundance of elements in the earth's crust varies from one element to other and is given in Table 1.1.

Table 1.1 Relative abundance of elements in the earth's crust

Element	Symbol	Atomic number	Abundance (%)
Oxygen	O	8	49.6
Silicon	Si	14	25.8
Aluminium	Al	13	7.4
Iron	Fe	26	4.6
Calcium	Ca	20	3.4
Sodium	Na	11	2.6
Potassium	K	19	2.4
Magnesium	Mg	12	1.9
Hydrogen	H	1	0.9
Titanium	Ti	22	0.6
Chlorine	Cl	17	0.2
Phosphorous	P	15	0.1

Note: Together, these elements constitute 99.5% of earth's crust and the remaining elements total 0.5%.

ILLUSTRATION 1.1

Give examples of (a) igneous and (b) sedimentary rocks. What is the origin of (a) igneous rocks and (b) sedimentary rocks?

Sol.

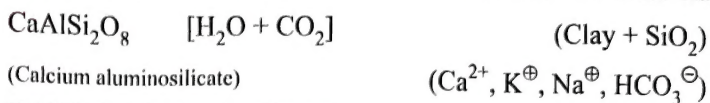
- Example of igneous rock is granite.
- Examples of sedimentary rock are chalk, sandstone, limestone.
- Origin of igneous rocks:** Solidified matter from magma on cooling forms igneous rocks.
- Origin of sedimentary rocks:** Sediments brought by rain or wind and deposited in rivers and lakes form sedimentary rocks.

1.1.1 OCEAN AS SOURCE OF ELEMENTS

Oceans are a rich source of many useful substances. Sea water, for example, contains nutrients and minerals. Oil and natural gas occur in continental shelf sediments. Metals such as gold and manganese

are found in sediments on the ocean floor. Sea water receives many of the dissolved salts by way of weathering of the earth's surface by rain water. This can be depicted by the following example:

Igneous rock + Rain water \longrightarrow Stream of water + Detritus clay



KAlSi_3O_8 (K aluminosilicate),
 $\text{NaAlSi}_3\text{O}_8$ (Na aluminosilicate).

Marine organisms convert Ca^{2+} ions into CaCO_3 (shells), which forms sediments. Hydrochloric acid ejected by undersea volcanoes reacts with HCO_3^- to form chlorides of Na, K and Ca in sea water. A few elements such as chlorine, bromine, sodium and magnesium are recovered from sea water. Also some rare metals are recovered from manganese nodules, which are occasionally found in seabed.

Vast quantities of metallic salts are also held in solution in the oceans, the principal ions being Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Sr^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , F^- , Br^- , and I^- . In the future, sea water may become an important source of many metals such as uranium and gold.

1.2 MODES OF OCCURRENCE OF ELEMENTS

Elements occur in nature either in the fresh (uncombined or native) state or in the combined state (as compounds). The reason for difference in mode of occurrence is difference in chemical reactivities.

1.2.1 NATIVE STATE

When an element is found free or in uncombined state, it is said to occur as native. These elements have little or no affinity for oxygen and resists the attack of water and other chemical reagents. Some elements found in the native state are copper (Cu), silver (Ag), gold (Au), mercury (Hg), platinum (Pt) etc.

1.2.2 COMBINED STATE

Elements which easily react with oxygen, moisture and other chemical reagents occur in the combined state, i.e. in form of their compounds. In the combined state, non-metals occur in the reduced form, i.e., X^- (where $\text{X}^- = \text{F}^-, \text{Cl}^-, \text{Br}^-$, etc.), whereas metals occur in the oxidised form i.e., oxides (e.g. Al_2O_3 , Fe_2O_3) etc.

1.3 MODE OF OCCURRENCE OF METALS

The naturally occurring materials in which metals or their compounds occur in the earth's crust are called **minerals**. Those minerals from which the metals may be extracted conveniently and economically are called **ores**.

All ores are minerals, but all minerals are not ores. For example, all clays contain aluminium but clay ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) is not considered an ore of aluminium, since the extraction of Al from clay is neither convenient nor economically viable. Thus, clay is an example of mineral. Whereas bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) is considered a ore of aluminium, since aluminium can be conveniently and economically extracted from bauxite.

1.3.1 CLASSIFICATION OF ORES

Based on their mode of occurrence, ores are classified as follows:

1. **Native ores:** These ores contain metals in the free state. Sometimes, lumps of almost pure metals are also found, which are known as **nuggets**.

Examples of native ores are copper (Cu), silver (Ag), and platinum (Pt).

2. **Combined ores:** These ores have metals occurring in simple or complex form as follows:

	Types of ore	Name of the ore	Composition of the ore
1.	Oxides	Corundum Diaspore Bauxite Tin stone Rutile Haematite Magnetite Limonite Chromite Cuprite (or ruby copper) Illmenite Zincite Pyrolusite	Al_2O_3 $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ SnO_2 TiO_2 Fe_2O_3 Fe_3O_4 $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ Cu_2O $\text{FeO} \cdot \text{TiO}_2$ ZnO_2 MnO_2
2.	Sulphides	Galena Zinc blende Cinnabar Argentite (or silver glance) Pyrargyrite (or ruby silver) Iron pyrites Copper pyrites Chalcocite (or copper glance)	PbS ZnS HgS Ag_2S $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_2$ FeS_2 CuFeS_2 or $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ Cu_2S
3.	Halides	Rock salt Horn silver Carnallite Fluorspar Cryolite Sylvine	NaCl AgCl $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ CaF_2 Na_3AlF_6 KCl
4.	Carbonates	Magnesite Limestone Dolomite Calamine Malachite Azurite Cerrusite Siderite	MgCO_3 CaCO_3 $\text{CaCO}_3 \cdot \text{MgCO}_3$ ZnCO_3 $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$ PbCO_3 FeCO_3

5.	Sulphates	Epsom salt or epsomite Barytes Gypsum Glauber's salt Kainite Celestine Chalcanthite Anglesite Anhydrite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ BaSO_4 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ SrSO_4 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ PbSO_4 CaSO_4
6.	Silicates	Petalite Beryl Willemite China clay Mica Felspar Talc Asbestos	$\text{LiAl}(\text{Si}_2\text{O}_5)_2$ (All are ores of Li) $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (All are ores of beryllium) Zn_2SiO_4 $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ KAlSi_3O_8 or $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ $\text{Mg}_2(\text{Si}_2\text{O}_5) \cdot \text{Mg}(\text{OH})_2$ $\text{CaMg}_3(\text{SiO}_3)_4$ or $\text{CaSiO}_3 \cdot 3\text{MgSiO}_3$
7.	Phosphates	Amblygonite Triphylite Chlorapatite Fluorapatite	$\text{LiF} \cdot \text{AlPO}_4$ $(\text{Li, Na})\text{PO}_4 \cdot (\text{Fe, Mn})_2(\text{PO}_4)_3$ $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Cl}$ $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$
8.	Nitrates	Saltpetre Chile saltpetre	KNO_3 NaNO_3
9.	Arsenides	Kupfernickel Nickel glance	NiAs NiAsS

ILLUSTRATION 1.2

- a. In general, which metals are expected to occur in the native state in nature?
- b. A certain metal M occurs in three compounds namely X, Y and Z. X has 15% of M, Y has 66% of M and Z has 71% of M. If we extract M from X, Y and Z, it costs Rs. 35 per kg, Rs. 45 per kg and Rs. 100 per kg respectively. Out of X, Y and Z which mineral can be considered as an ore of M?

Sol.

- a. The elements which lie below hydrogen in the electrochemical series are expected to occur in the nature in the native state. For example, Cu, Ag, Au, Pt etc.
- b. All three X, Y and Z are minerals as they contain M, but all cannot be called ores. Extraction of M from mineral X would cost less but result in a very less amount. Similarly, extraction from Z would result in large amount, but it will also cost a large sum. Hence Y is the appropriate mineral from which M should be extracted as it would give sufficient amount and would not even cost much.

1.3.2 FACTORS ON WHICH MODE OF OCCURRENCE DEPENDS

Mode of occurrence depends on the following factors:

1. Enthalpy of formation
2. Electrode potential
3. Size, charge, polarisability—HSAB principle

1. Enthalpy of formation ($\Delta_f H^\ominus$): Standard enthalpy of formation for some compounds of calcium is as follows:

Compound	$\Delta_f H^\ominus$ (kJ mol ⁻¹)	Ore
Ca ₃ (PO ₄) ₂	-4126	Phosphorite
CaF ₂	-1214	Fluorspar
CaCO ₃	-1207	Calcite
CaCl ₂	-795	—
CaO	-635	—
CaS	-483	—

For a compound to exist as mineral, it should be stable, i.e. should not be attacked by moisture, O₂ or CO₂. The compound should be thermally stable. Considering the value of $\Delta_f H^\ominus$, the probability of finding Ca as calcium phosphate is maximum. CaCl₂, CaO, CaS do not occur as they are not stable towards water. But it is not always possible that a compound which is maximum stable should occur in nature, as will be discussed later on. Even if a very stable compound is present, it may not be profitable to use it as an ore. Because if it very stable, it is difficult to extract metal from that compound.

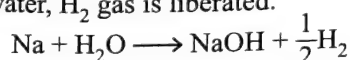
Element	$\Delta_f H^\ominus$ (kJ mol ⁻¹)				
	Car-bonate	Chloride	Oxide	Sul-phide	Ores
Na	-1131	-411	-416	-373	NaCl (Rock salt)
Al	—	-695	-1669	-509	Al ₂ O ₃ ·2H ₂ O (Bauxite)
Zn	-812	-416	-348	-203	ZnCO ₃ (Zinc blende)
Fe	-748	-405	-822	-178	Fe ₂ O ₃ (Haematite)
Au	—	+118	+80.8	—	Free state

Na should occur in nature as Na₂CO₃, as it is most stable, but it occurs as NaCl because of the conditions in nature. Al occurs as alumina as its oxide is most stable, and Al is extracted from this compound. Au cannot occur in nature in the combined state due to the high positive value of $\Delta_f H^\ominus$. Hence Au compounds are not stable.

- 2. Electrode potential:** E^\ominus value of H is 0.0V. In the emf series, the elements above H are electropositive. They can replace H from the acidic solution, hydrogen gas from water. They are easily converted to ions.



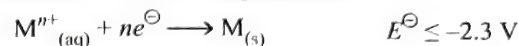
This value shows that the moment Na comes in contact with water, H₂ gas is liberated.



Therefore, Na cannot exist in free state in native. Au can exist in free state because Au cannot replace H₂ from H₂O, as it lies

below H in the emf series. Similarly, Cu and Ag also occur in nature in native state. By making use of standard electrode potentials, it is inferred that

- a.** Highly electropositive metals are those for which standard electrode potential value is less than or equal to -2.3 V, with reference to the following reaction:



For example,

	Li [⊕] /Li	K [⊕] /K	Ba ²⁺ /Ba
E^\ominus (V)	-3.04	-2.92	-2.90

	Ca ²⁺ /Ca	Na [⊕] /Na	Mg ²⁺ /Mg
E^\ominus (V)	-2.87	-2.71	-2.37

- b.** Moderately electropositive metals have standard electrode potential value between -0.44 V and -2.3 V.

For example,

	Al ³⁺ /Al	Ti ²⁺ /Ti	Mn ²⁺ /Mn
E^\ominus (V)	-1.66	-1.63	-1.16

	Zn ²⁺ /Zn	Fe ²⁺ /Fe
E^\ominus (V)	-0.76	-0.44

- c.** Weak or very weak electropositive metals having standard reduction potential values greater than -0.44 V.

For example,

	Ni ²⁺ /Ni	Pb ²⁺ /Pb	Cu ²⁺ /Cu
E^\ominus (V)	-0.25	-0.13	+0.34

	Ag [⊕] /Ag	Au ³⁺ /Au
E^\ominus (V)	-0.80	+1.5

From the above values, it can be inferred that Cu, Ag and Au can exist in nature in free state.

Another aspect of E^\ominus value is to predict probable oxidation state of a particular metal amongst the others under similar conditions. Only that oxidation state is possible which is thermodynamically stable.

- 3. HSAB principle:** Mode of occurrence of metals in a particular compound can also be predicted by using Hard Soft Acid Base (HSAB) principle. Soft acids form stable compounds with soft bases, while hard acids form stable compounds with hard bases. Borderline acids, i.e., metals in between hard acids and soft acids have preference for both soft and hard bases. For example,

- a.** Ca²⁺, Mg²⁺, Ti⁴⁺ and Al³⁺ occur as CaCO₃, MgCO₃, TiO₂, and Al₂O₃, respectively. Ca²⁺, Mg²⁺, Ti⁴⁺, and Al³⁺ are hard acids, while CO₃²⁻ and O²⁻ are hard bases.
- b.** Cu²⁺, Ag[⊕] and Hg²⁺ occur as sulphides namely CuS, AgS, and HgS since Cu²⁺, Ag[⊕] and Hg²⁺ are soft acids, while S²⁻ is a soft base.

1.4 EXTRACTION OF ELEMENTS

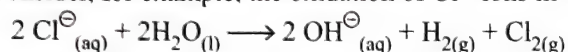
As already discussed, very few elements occur in the native state in nature. In the combined state, metals are usually found in the oxidised form (e.g., Fe₂O₃, MnO₂, SnO₂) while non-metals

are present in the reduced form such as X^\ominus ($X^\ominus = \text{Cl}^\ominus, \text{Br}^\ominus, \text{I}^\ominus$). The methods of extraction or isolation of metals and non-metals from natural sources are, therefore, quite different. Metals have to be free from their oxidised forms by reduction, while non-metals are obtained by oxidation. Their extractions are accordingly treated separately here. Reduction is brought about by electronation, i.e. by providing electron directly or indirectly, while oxidation is carried out by de-electronation i.e. by removing electron, directly or indirectly.

1.4.1 EXTRACTION OF NON-METALS

Non-metals occurring in the combined form are generally extracted by oxidation. Among non-metals, halogens are most important.

Consider, for example, the oxidation of Cl^\ominus ions in water:



The oxidation of Cl^\ominus ions to chlorine cannot be brought about by ordinary chemical methods. The oxidation of Cl^\ominus is accomplished by electrolysis. The minimum potential difference required for this is 2.2 V. Similarly, fluorine is also extracted by electrolysis. Elements like oxygen, nitrogen and noble gases are available from air. Carbon, sulphur and phosphorus are extracted either from native ores or by oxidation from their compounds occurring in nature. Since there is no general method of extraction of non-metals individual cases will be considered at the appropriate places in the text.

1.4.2 EXTRACTION OF METALS—METALLURGY

Metals are usually extracted from their ores by reduction processes, except in cases where the metals are unreactive ones. Before an ore is subjected to reduction, it needs to be subjected to various other processes/operations, such as concentration, calcination, etc.

The process of extracting metals from their ores and refining them is called **metallurgy**. (as shown in Fig. 1.1)

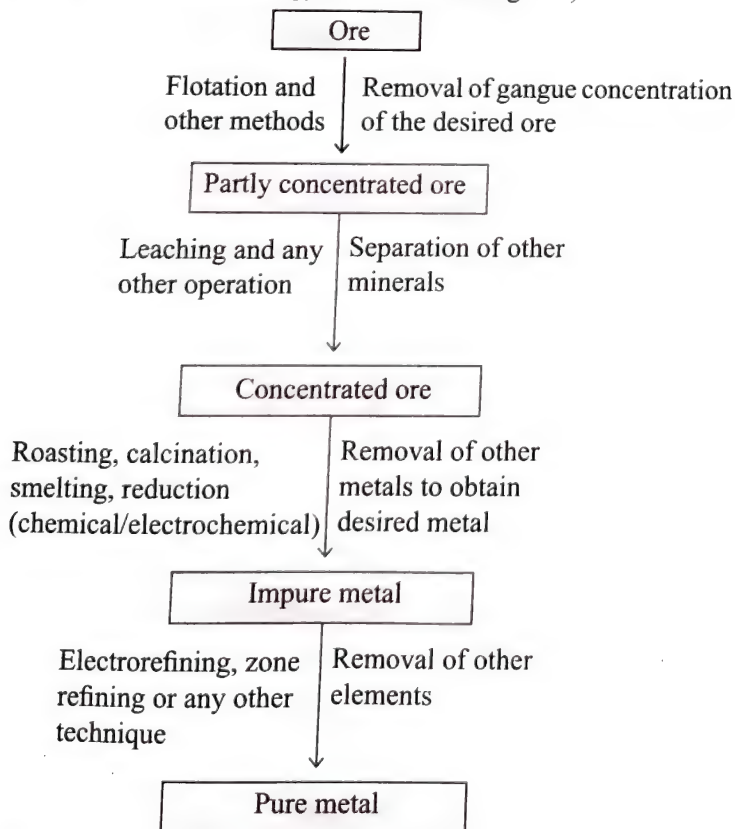


Fig. 1.1 Flow sheet for general metallurgical operation; the functions of processes are given on the right side, and the methods employed are given on the left

The process of extraction of a metal depends on the nature of the ore and chemical properties of the metal. Since different metals have different physical and chemical properties, the method of extraction varies from one metal to another. Hence, a single universal method cannot be applied for the extraction of all the metals. Different metallurgical operations are employed in the extraction of metals, and these are listed as follows:

1. Grinding and pulverising the ore.
2. Concentration of the ore (ore-dressing).
3. Reduction of the concentrated ore to crude metal.
4. Refining of the crude metal.

Various methods are available for each of these stages. The choice of the method employed depends on the type of impurity present, type of the metal, available facility, etc. All these metallurgical operations are discussed as follows:

1.4.3 GRINDING AND PULVERISING

Ores as obtained from the earth's crust usually occur in the form of big lumps. These lumps are broken or crushed into small pieces by means of jaw crushers or grinders. The process is known as **grinding**.

The small pieces thus obtained are reduced to fine powder with the help of ball mill or stamp mill. This process is known as **pulverisation**.

1.4.4 CONCENTRATION OF THE ORE (ORE-DRESSING)

Metallic ores as obtained from the earth's crust are often mixed with non-metallic and rocky materials such as clay, sand, limestone, etc. The impurities present in the metallic ores are called **gangue or matrix**. The process of removal of the gangue from the ore is called **concentration of the ore-dressing or benefaction process** and the purified ore is called **concentrate**. Some important methods for ore-dressing are as follows:

1.4.4.1 Hand Picking

When the impurities present are quite distinct from the ore so that they can be easily differentiated by our eyes, picking by hand is done.

1.4.4.2 Hydraulic Washing or Gravity Separation Method

Principle: It is based on the difference in the specific gravity of the metallic ore and the gangue particles. This method is used mainly for heavier ores such as cassiterite (SnO_2), haematite (Fe_2O_3).

Working: Powdered ore is treated with a stream of running water; gangue particles which are lighter (as compared to metallic ore) are washed away, while the heavier ore particles are left behind. This is known as **levigation**. Two common methods for hydraulic washing are as follows:

1. **Wilfley table method:** This process involves the use of sloping wooden table. The wooden table has a slanting floor on which long wooden strips called cleats as rifles are fixed. The crushed ore is fed onto the top of the table, which is kept vibrating all the time. A running water stream is made to flow across the table at right angles to the slope. The lighter siliceous and earthy gangue particles rise up and are carried away, while heavier particles settle at the bottom.

- 2. Hydraulic classifier method:** Hydraulic classifiers (Figure 1.2) consists of a conical reservoir fitted with hopper at the top and pipe at the bottom. Powdered ore is dropped from the hopper and a powerful stream of water is forced in through the pipe below. Lighter gangue particles are carried away by the current of water and heavier ore particles collect at the apex of the cone. The conical shape helps in reducing the velocity of water and thus ore particles are prevented from being carried away by water.

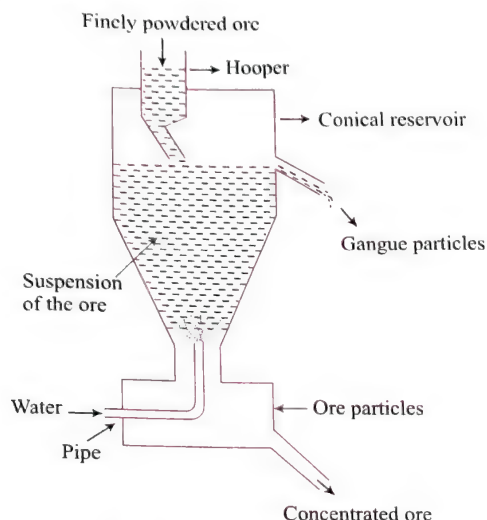


Fig. 1.2 Hydraulic classifier

1.4.4.3 Electromagnetic Separation Method

Principle: This method is based on magnetic and non-magnetic properties of the ore and gangue, respectively. This method can be used when the ore is magnetic (attracted by the magnet) and gangue is non-magnetic. This method can be used to separate:

1. Chromite, $\text{Fe}(\text{CrO}_2)_2$, from siliceous impurities. Chromite is magnetic, whereas siliceous impurities are non-magnetic.
2. Mixture of Wolframite (FeWO_4) and cassiterite (SnO_2). Wolframite is magnetic, whereas cassiterite is non-magnetic.
3. Mixture of rutile (TiO_2) and chloroapatite, $[\text{CaCl}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2]$. Rutile is magnetic, whereas chloroapatite is non-magnetic.

Working: This method involves the use of electromagnetic separator. The separator consists of leather or brass belt moving over two rollers, one of which encloses magnet in it. The powdered ore is dropped on this moving belt. The magnetic component gets attracted by the magnet and falls just below it, whereas the non-magnetic component falls away from it, as shown in Fig. 1.3.

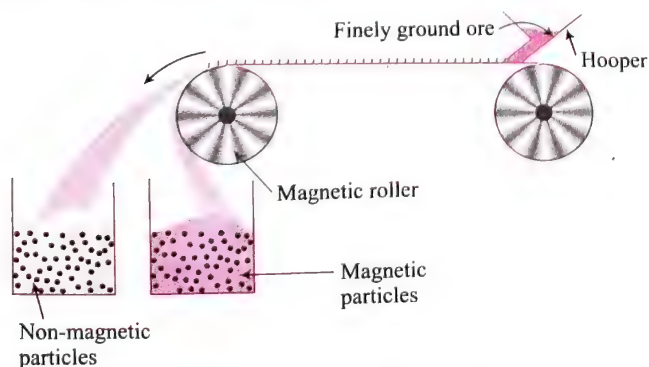


Fig. 1.3 Electromagnetic separation

1.4.4.4 Froth Flotation Method

Principle: This method is based on different wetting characteristics of the ore and gangue by oil and water. Ore is preferentially wetted by oil, whereas gangue is preferentially wetted by water.

This method is extensively employed for concentration of sulphide ores, e.g., galena (PbS), copper pyrites (CuFeS_2) and zinc blende (ZnS).

Working: A suspension of finely powdered ore with water is made. Depending on the nature of the ore, various additives such as frothers, froth stabilisers and collectors are added to the above suspension.

Frothers such as pine oil help in the formation of froth.

Froth stabilisers such as cresols and aniline help in stabilising the froth.

Collectors such as ethyl xanthate, potassium ethyl xanthate, and fatty acids help in enhancing the non-wettability of the mineral particles. These attach themselves by polar groups to the grain of minerals, which then become water repellent and pass on to the froth.

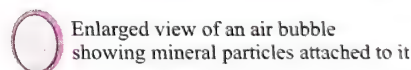
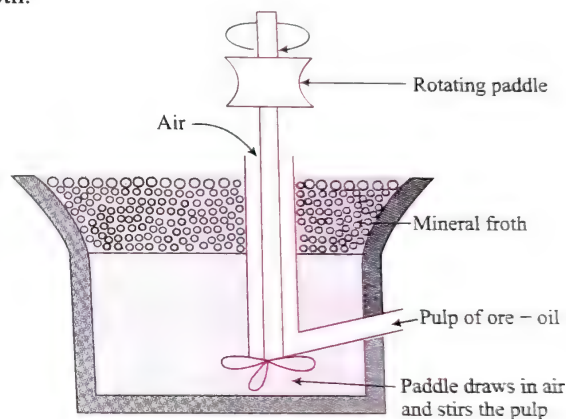
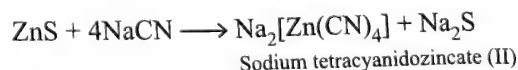


Fig. 1.4 Froth flotation method

A rotating paddle (Figure 1.4) agitates the suspension and draws in air causing the formation of the froth, which carries with it the mineral particle. The froth being lighter floats to the surface and is skimmed off. It is allowed to collapse and dry for recovery of mineral particles.

By adjusting the proportion of oil to water, it is often possible to separate one sulphide ore from another. One more additive, **depressants or activators**, is added to prevent certain type of sulphide ore particles from forming the froth with the bubbles. Thus, it helps in the separation of different minerals present in the same ore. For example, galena (PbS) is usually associated with zinc blende (ZnS). In this case, froth flotation process is carried out by using a depressant (NaCN).

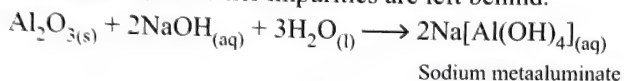
NaCN (depressant) depresses the flotation property of ZnS and FeS_2 grains, so that PbS passes into the froth when air is blown in. This is due to the reason that NaCN reacts with ZnS , thus forming a zinc complex $\text{Na}_2[\text{Zn}(\text{CN})_4]$ on the surface of ZnS , thereby preventing it from forming the froth. Under these conditions, only PbS forms froth and hence is separated from ZnS ore.



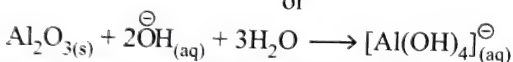
1.4.4.5 Leaching or Hydrometallurgy

Principle: Leaching depends on the difference in chemical properties of the ore and gangue. Leaching involves the treatment of finely powdered ore with a suitable reagent (acids, bases or other chemicals), which can selectively dissolve the ore but not gangue. The metal is then recovered from its salt solution either by its electrolysis or by adding some electropositive metal to it when the metal to be extracted is obtained as a precipitate. Some important examples are described below:

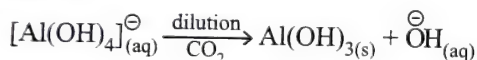
- 1. Leaching of bauxite (Bayer's process):** In Bayer's process, pure alumina (Al_2O_3) is obtained from the bauxite ore. Impurities usually associated with the bauxite ore are iron (III) oxide (Fe_2O_3), silica (SiO_2) and titanium oxide (TiO_2). The powdered ore is treated with concentrated solution of NaOH (45%) at 473–573 K. Al_2O_3 dissolves forming sodium metaaluminate, and other impurities are left behind.



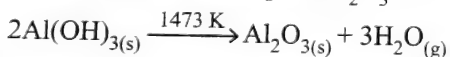
or



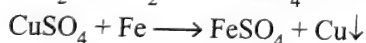
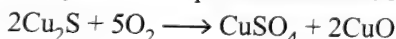
The solution containing sodium metaaluminate is filtered, and the filtrate is cooled and its pH is adjusted downward by dilution and/or neutralisation with carbon dioxide (CO_2), when aluminium hydroxide $[\text{Al}(\text{OH})_3]$ is precipitated. Seeding with a little freshly precipitated aluminium hydroxide quickens the process.



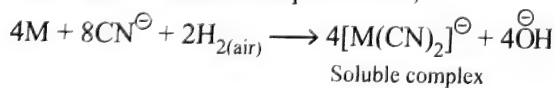
The precipitate of $\text{Al}(\text{OH})_3$ is filtered, dried and finally heated to about 1473 K to obtain pure Al_2O_3 .



- 2. Extraction of copper (Cu):** Large heap of copper glance, Cu_2S , is exposed to air and water. In about a year, the ore Cu_2S is oxidised to CuSO_4 . The solution of CuSO_4 is either electrolysed or scrap iron is added to it to get Cu as precipitate.

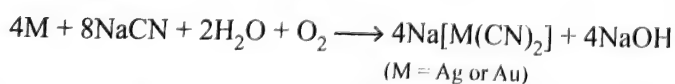


- 3. Leaching of silver and gold ores (MacArthur and Forest's cyanide process):** Leaching is also employed in concentrating silver and gold ores. In this process, the finely powdered ore argentite (Ag_2S) or the native silver or gold is treated with dilute solution of NaCN or KCN and a current of air is continuously passed into the solution. As a result, the precious metals are converted into soluble complex. Thus,

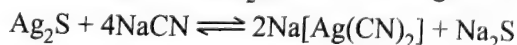


(where M = Ag or Au)

or

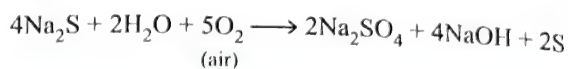


In case of ore argentite (Ag_2S), the following reaction takes place:



The above reaction is a reversible reaction, but when current of air is passed into the solution, Na_2S formed in the above reaction

is oxidised to Na_2SO_4 , hence the reaction proceeds in the forward direction.



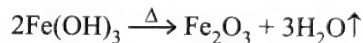
1.4.5 REDUCTION OF CONCENTRATED ORE TO THE METALLIC OXIDE

The concentrated ore needs to be converted into a form which is suitable for reduction to the metal. Metals are usually present in ores as hydroxides (hydrated oxide), carbonates or sulphides. These ores are subjected to either calcination or roasting/smelting, depending upon the nature of the minerals present in the ore, and thereby converted to the oxide form. For thermodynamic reasons, it is easier to reduce an oxide than the sulphide ore.

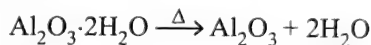
1.4.5.1 Calcination

Calcination is the process in which the ore is heated strongly in absence or limited supply of air at a temperature that the ore does not melt. This ensures the removal of:

1. Volatile impurities such as moisture, CO_2 , SO_2 , organic matter

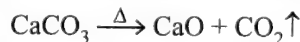


2. Water from hydrated ore

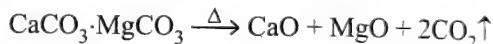


Bauxite

3. Carbon dioxide from carbonate ore



Limestone



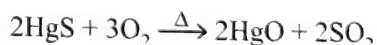
Dolomite

Calcination is usually done in reverberatory furnace. It makes the mass porous so that it can be easily reduced to metallic state in the next step of metallurgy.

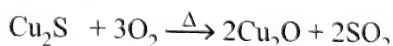
1.4.5.2 Roasting

Roasting is a process in which the ore (usually sulphide) is heated strongly in presence of air, at a temperature below the melting point of the ore. This step ensures:

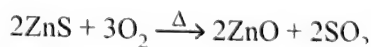
1. Conversion of the ore to the oxide form



Cinnabar

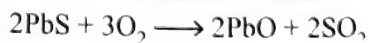


Copper glance

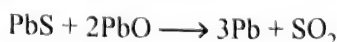


Zinc blende

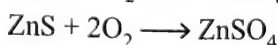
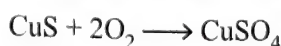
Sometimes, a part of the sulphide may act as reducing agent as in the case of extraction of lead.



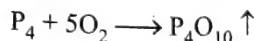
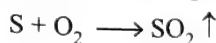
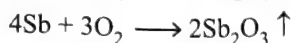
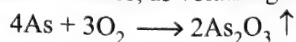
Galena



Sometimes, insoluble sulphide ores are converted to corresponding sulphate ore, which are water soluble.



2. Removal of non-metallic impurities such as arsenic (As), antimony (Sb), sulphur (S) and phosphorous (P), which are oxidised to oxides, as volatile gases.



3. Removal of water from hydrated ores.

4. Makes the ore porous so that it undergoes easier reduction in the next step of metallurgy.

Roasting is usually done in reverberatory furnace or blast furnace (Figure 1.5).

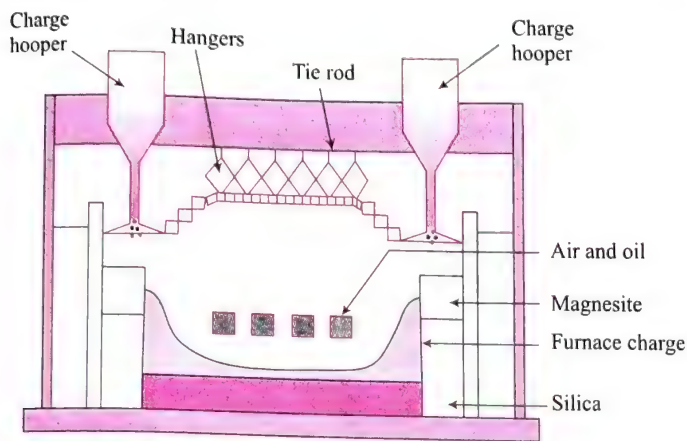


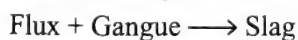
Fig. 1.5 Section of a modern reverberatory furnace

During roasting, air vents are kept open, whereas during calcination, air vents are either completely or partially closed.

1.4.6 REDUCTION OF ROASTED/CALCINED ORE TO METAL

The extraction of a metal from its oxide by a process involving melting is known as **smelting**. If the roasted/calcined ore still contains non-fusible impurities of earthy matter (such as silica-silicates, metallic oxides, etc.), an additional substance is added to the furnace charge (roasted/calcined ore and coke) during the process of smelting to remove them. This additional substance is known as **flux**.

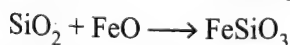
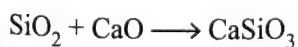
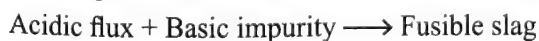
During smelting, flux combines with non-fusible impurities (gangue) and forms **slag**, a fusible material.



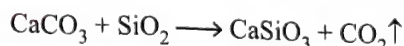
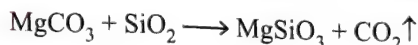
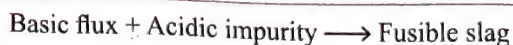
Slag, being lighter than molten metal, floats on the molten metal, from where it can be easily removed. At high temperature, slag is a liquid, which is insoluble in the molten metal.

Types of fluxes: Fluxes are of two types:

1. **Acidic fluxes:** Acidic fluxes such as silica (SiO_2) and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) are added to the basic impurities, such as, metallic oxides (such as CaO , FeO), hence removing them as fusible slag.



2. **Basic fluxes:** Basic fluxes such as limestone (CaCO_3), magnesite (MgCO_3) and haematite (Fe_2O_3) are added to remove acidic impurities such as silica (SiO_2) as fusible slag.



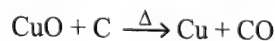
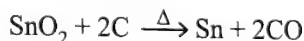
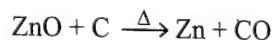
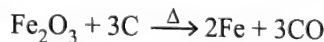
In general, most of the metals which occur in the combined state are present in their positive oxidation states. They must therefore be reduced by electronation, providing electrons to become free metals. The nature of reducing agent to be used in a particular case depends on how difficult the reduction process is. If the metal is very reactive like the alkali metals, alkaline earth metals and aluminium, they can be reduced only by the electrolytic method. Less reactive metals such as copper, lead, tin, etc. can be reduced by chemical reducing agents. The choice of the reducing agent is decided by the factors of energetics and economics. Various reduction processes are described as follows:

1. Chemical reduction
2. Auto-reduction or self-reduction
3. Electrolytic reduction

1.4.6.1 Chemical Reduction

Carbon as reducing agent: Carbon can be used as reducing agent for extraction of lead (Pb), zinc (Zn), copper (Cu), tin (Sn).

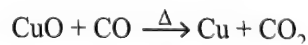
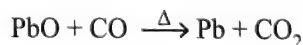
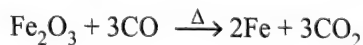
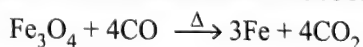
Roasted oxide ore is mixed with carbon (charcoal, coke or coal) and a flux and heated to a high temperature in a suitable furnace.



In case of zinc, which is volatile at the temperature at which reduction is being carried out, reduction cannot be done in open furnace.

Reduction by using carbon cannot be done in the cases where the free metal formed has tendency to form carbide, i.e. metal has more affinity for carbon as compared to oxygen.

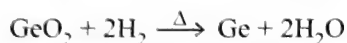
Carbon monoxide as reducing agent: In some cases, CO produced in the furnace itself acts as reducing agent.



Production of iron from the oxide ore: The extraction of iron, the most important industrial metal, is carried out in a blast furnace. The charge consists of iron ores (haematite Fe_2O_3 and magnetite Fe_3O_4), coke and limestone, which is heated with a blast of air. As the exothermic reaction proceeds, a composition and temperature gradient is set up in the furnace. Below 1123 K, CO reduces the ores to FeC. Reduction to Fe by CO can occur at about 1123 K and that direct reduction, in which the reducing agent is C, can occur at about 1123 K. In this region, limestone also decomposes to CaO and CO_2 and slag formation takes place.

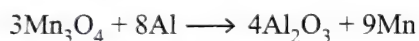
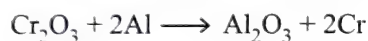
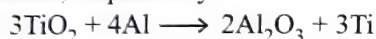
Note: Apart from the integrated steel plants that produce steel out of pig iron from blast furnaces, steel is also produced by electric arc furnaces and induction furnace units using steel scrap, sponge iron as feed material. While integrated steel plants produce mainly mild steel in bulk quantities, the electric steel-making units produce mild steel as well as alloy steel, including stainless steel.

Hydrogen as reducing agent: Hydrogen gas (H_2) is difficult to use because of its inflammable nature.

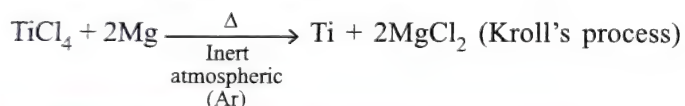
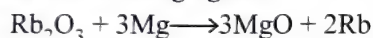


Aluminium as reducing agent: Aluminium powder is used to reduce metallic oxides to metal. The process is known as aluminothermic process or Goldschmidt thermic process. It is a strong exothermic reaction.

Metallic oxides such as TiO_2 , Cr_2O_3 , and Mn_3O_4 are reduced to Ti, Cr, and Mn, respectively.



Magnesium as reducing agent:

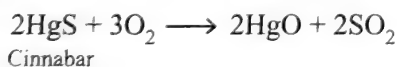


1.4.6.2 Auto-reduction or Self-reduction Process

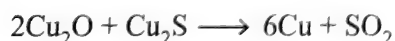
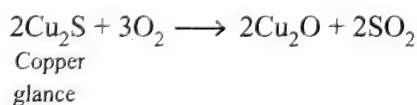
In certain cases, no reducing agent is required. The sulphides of less electropositive metals such as mercury (Hg), copper (Cu), lead (Pb), tin (Sn) are reduced without the use of any additional reducing agent.

When the ores are heated in air, a part of these ores is changed into the oxide or sulphate, which then reacts with the remaining part of the ore, to give the metal and SO_2 as shown below:

1. Extraction of mercury from cinnabar (HgS)

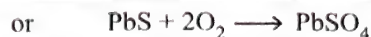
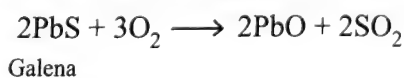


2. Extraction of copper from copper glance (Cu_2S)



Copper (Cu) so obtained is known as **blister copper** because as it solidifies, SO_2 hidden in it escapes out producing blisters on the surface.

3. Extraction of lead from galena (PbS)



Elevated temperature and the anion/s associated with the metal may bring about this change.

All roasting/smelting processes mentioned above make use of reverberatory furnaces at some stage. Oil burners shoot along intensely hot flame down the furnace and melt the charges. On the walls there are suitable tap holes for crude metals and the slag. Such a furnace may melt upto 106 kg of charge per day. Smelting operations can also be carried out in converters. Air is blown through the molten material, when the impurities are largely removed as volatile oxidation products. Also magnesite linings are used in converters to slag off any metallic impurities. Converters may be of two types:

1. **Bessemer converter**, similar to that used in metallurgy of iron.
2. **Peirce-Smith converter**, which consists of a large horizontal steel drum resting upon rollers. Rolls of steel tubes (tuyeres) pass into the converter and are connected to an air duct. Air is forced into the molten bath of crude metal. The process provides its own heat due to the oxidation of impurities and the temperature rises to ~ 2673 K.

1.4.6.3 Electrolytic Reduction Method

When the chemical reduction method is not applicable, electrolytic reduction is done. Electrolytic reduction is of two types:

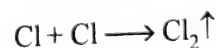
1. Reduction at high temperature in the absence of water; molten electrolyte is used.
2. Electrolysis at low temperature using water hydrometallurgy. Cost factor is low.

Reduction at high temperature is mainly used for alkali and alkaline earth metals Zn and Al. Their oxides are very stable and hence in order to reduce their oxides to free metal, they have to be heated at a very high temperature with carbon. But at a high temperature, these metals react with carbon to form carbides. Thus, such metals cannot be extracted by reducing their oxides with carbon. These are, however, extracted by electrolysis of their oxides, hydroxides or chlorides in fused state. The metal is liberated at the cathode. Some other salt has to be added to lower down the melting point of the compound taken. For example,

1. **Extraction of Na** by the electrolysis of fused mixture of $NaCl$ and $CaCl_2$ by Down Process. [For details, refer "Inorganic Chemistry for Joint Entrance Examination JEE (Advanced) Part I" by K. S. Verma Chapter 4, Section 4.9.1] Various reactions taking place in the electrolytic cell are as follows:



Electrolysis:



Hence at cathode, Na metal is discharged, whereas at anode, Cl_2 gas is discharged. The products react rapidly and hence suitable arrangements are made to keep them separate. CaCl_2 is added in the above process as:

- It lowers down the melting point of NaCl .
- Discharge potential of Ca^{2+} is much higher than Na^{\oplus} , hence Na^{\oplus} is discharged.

- Extraction of Al:** AlCl_3 is not chosen; rather, Al_2O_3 is chosen, since AlCl_3 is a covalent compound and does not conduct electricity. Al_2O_3 is a high melting compound and hence cryolite, $(\text{Na}_3\text{AlF}_6)$ is added to it. It dissolves Al_2O_3 . This dissolution is easily done at $700\text{--}1000^\circ\text{C}$. Graphite electrodes are used for the removal of Al.

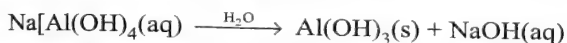
1.4.6.4 Aluminium Metal Extraction from Bauxite

Aluminium metal is extracted from bauxite in a two-stage process. In the first stage, pure alumina (Al_2O_3) is obtained from bauxite and in the second stage, electrolysis of Al_2O_3 in molten cryolite (Na_3AlF_6) is carried out to obtain aluminium metal.

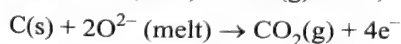
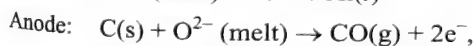
Bauxite contains SiO_2 , iron oxides and titanium (IV) oxide as impurities. The bauxite ore is digested with a concentrated solution of sodium hydroxide at $473\text{--}523\text{ K}$ and $35\text{--}36$ bar pressure. Aluminium oxide and silica dissolve to form sodium aluminate and sodium silicate respectively leaving behind iron oxide and TiO_2 which are filtered off.



The filtrate containing sodium aluminate and sodium silicate is diluted and seeded with freshly precipitated aluminium hydroxide which induces the precipitation of aluminium hydroxide leaving behind sodium silicate in solution.



The aluminium hydroxide is filtered, dried and calcined at 1473 K to yield pure alumina. Aluminium is obtained from alumina by electrolysis; this is known as **Hall-Heroult process**. The modern electrolysis process uses synthetic cryolite, Na_3AlF_6 . Typical electrolyte composition ranges are Na_3AlF_6 (80–85%), CaF_2 (5–7%), AlF_3 (5–7%), Al_2O_3 (2–8%) intermittently recharged. The electrolysis of this mixture is carried out in an electrolytic cell (schematically shown in figure) using carbon electrodes. The oxygen liberated at the anode reacts with the carbon anode producing CO and CO_2 . The overall reactions may be written as:



- The electrode potential in aqueous system as given in emf series for the reduction of metal ions differs from the potential needed for the deposition of metal in molten state.
- Electrode potential in aqueous system is largely influenced by hydration enthalpies, whereas in molten state, these are absent.
- In molten state, ions are in direct influence with each other, and there is no hydration sphere.
- In both the cases, ionisation enthalpies are of great significance.

- Decomposition potential in molten state is temperature dependent.

Discharge potential, i.e., the potential at which a metal is discharged at cathode depends on:

- Position of metal in electrochemical series:** Lower the E^\ominus value, lower is the discharge potential.
- Concentration of the metal ions in the electrolyte:** Greater the concentration, lower is the discharge potential.

ILLUSTRATION 1.3

- Metal sulphides occur mainly in rocks and metal halides occur in lakes and seas. Give reason.
- Pine oil is used in froth flotation process. Why?
- What is a depressant? Give an example.
- What is the role of stabiliser in froth flotation process?
- What is gangue?

Sol.

- Metal halides being soluble in water get dissolved in rain water and are carried to lakes and seas during weathering of rocks. On the other hand, metal sulphides being insoluble are left behind in the rocks as residue.
- Pine oil increases the non-wetability of ore particles by water, i.e., ore particles are preferentially wetted by pine oil and hence become lighter and rise to the surface along with the froth.
- Depressants are compounds which prevent the formation of froth in froth flotation process. For example, NaCN acts as a depressant for ZnS in the separation of ZnS ore from PbS ore.
- Chemical compounds namely aniline and cresols, which tend to stabilise the froth in froth flotation process, are called froth stabilisers.
- The earthy and siliceous impurities associated with ores is called gangue.

ILLUSTRATION 1.4

- Metals occur in the native form because of their
 - High electronegativity
 - Low reactivity
 - Low density
 - High reactivity
- Specific gravity of slag is
 - Higher than molten metal
 - Same as that of molten metal
 - Less as that of molten metal
 - None of the above
- Which process is used for the extraction of metals from their sulphide ores?
 - Smelting
 - Froth flotation
 - Electrolysis
 - Metal displacement
- Calamine is an ore of
 - Hg
 - Zn
 - Ca
 - Cd
- Non-fusible impurities of ores are removed by adding
 - Slag
 - Flux
 - Gangue
 - None

6. Common method of extraction of metals from oxide ore involves
 - a. Reduction with aluminium
 - b. Reduction with carbon
 - c. Reduction with hydrogen
 - d. Electrolytic method
7. Smelting is the reduction of oxide to metal by
 - a. Carbon
 - b. Hydrogen
 - c. Aluminium
 - d. Electric current
8. During froth flotation process, commonly used frother is
 - a. CuSO_4
 - b. NaCN + alkali
 - c. Pine oil
 - d. Potassium xanthate
9. Iron ores are dressed by
 - a. Froth flotation process
 - b. Hand picking
 - c. Magnetic separation
 - d. All of the above
10. Silicon is the main constituent of
 - a. Alloys
 - b. Rocks
 - c. Animals
 - d. Plants

Sol. 1. b 2. b 3. b 4. b 5. b
 6. b 7. a 8. c 9. c 10. b

CONCEPT APPLICATION EXERCISE 1.1

1. Why is Fe an abundant element on earth, and why are the elements with higher atomic number increasingly rare?
2. Name the chief forms of the occurrence of the following in the earth's crust:
 - a. Aluminium
 - b. Calcium
 - c. Sodium
 - d. Lead
3. Outline the principles of refining of metals by the following methods:
 - a. Electrolytic refining
 - b. Zone refining
 - c. Vapour phase refining
4. Predict the modes of occurrence of the following three types of metals:
 - a. Highly reactive (e.g. Na)
 - b. Moderately reactive (e.g. Fe)
 - c. Noble metal (e.g. Au)
5. Why metal ores are not found as their nitrates?
6. During the reduction of TiCl_4 by magnesium why helium not nitrogen is preferred?
7. Write the name and chemical formula of an ore of tungsten which contains tungstate ion.
8. (i) Name the process used in the manufacture of steel from spiegel and (ii) the alloy of spiegel.
9. Hydrometallurgy, pyrometallurgy and electrometallurgy are used for the extraction of which metals.
10. Name the process and metal used in large scale extraction of Cr and Mn.
11. Why a sulphide ore of copper is heated in a furnace after mixing with flux?
12. How wrought iron is obtained from cast iron?
13. How the impurities of S, Si, and P are removed from cast iron?
14. How ZnS and PbS are separated by froth flotation process?

1. Selecting the element which will be the most suitable reducing agent for a particular oxide during a metallurgical operation.
2. Predicting the optimum temperature at which the reduction can occur smoothly.

For any reaction or process, Gibb's free energy change (ΔG) is given by the equation

$$\Delta G = \Delta H - T\Delta S \quad \dots (i)$$

where ΔH = enthalpy change,

ΔS = entropy change and

T = absolute temperature.

The free energy change is also related to the equilibrium constant, K of the reaction at temperature T by the following equation

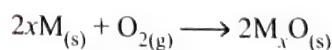
$$\Delta G = -RT \ln K \quad \dots (ii)$$

For any reaction to be feasible at any temperature, ΔG must be negative. In Eq. (i), if ΔG is -ve, K will be +ve. This means that the reaction will proceed to form the products. One can conclude the following:

1. Greater the -ve value of ΔG , more spontaneous is the reaction. ΔG will be negative when
 - a. $\Delta H = -\text{ve}$ and $T\Delta S = +\text{ve}$ (At any temperature)
 - b. $\Delta H = -\text{ve}$ and $T\Delta S = -\text{ve}$ (Temperature should be low)
 - c. $\Delta H = +\text{ve}$ and $T\Delta S = +\text{ve}$ ($T\Delta S > \Delta H$ and temperature should be high)
2. A reaction with +ve value of ΔG can still be made to occur if it is coupled with another reaction having a high -ve value of ΔG , so that the net ΔG of both the reactions is -ve. Above-mentioned coupling reaction can be easily understood using Ellingham diagram.

1.5.1 ELLINGHAM DIAGRAM

Ellingham diagram usually consists of plots of $\Delta_f G^\ominus$ vs T for the formation of oxides of various elements. Similar diagrams can also be drawn for sulphides and halides of various elements. These diagrams can be used to predict the feasibility of thermal reduction of an ore. For example, consider the formation of metal oxide (M_xO).



In this reaction, O_2 , a gas, is used up and $\text{M}_x\text{O}_{(s)}$, a solid is formed. Since gases have higher entropy than solids, ΔS becomes negative. Thus, on increasing the temperature, $T\Delta_f S^\ominus$ becomes more negative.

In the equation $\Delta_f G^\ominus = \Delta_f H^\ominus - T\Delta_f S^\ominus$; $T\Delta S$ is subtracted, hence $\Delta_f G^\ominus$ becomes less and less negative, i.e., $\Delta_f G^\ominus$ increases with increase in temperature. In other words, lines in $\Delta_f G^\ominus$ vs T plot have +ve slopes for most of the reactions involving the formation of metal oxides. The following observations are made from the $\Delta_f G^\ominus$ vs T diagram (Figure 1.6).

1.5 THERMODYNAMICS OF METALLURGY

The basic concept of thermodynamics is useful in the following ways:

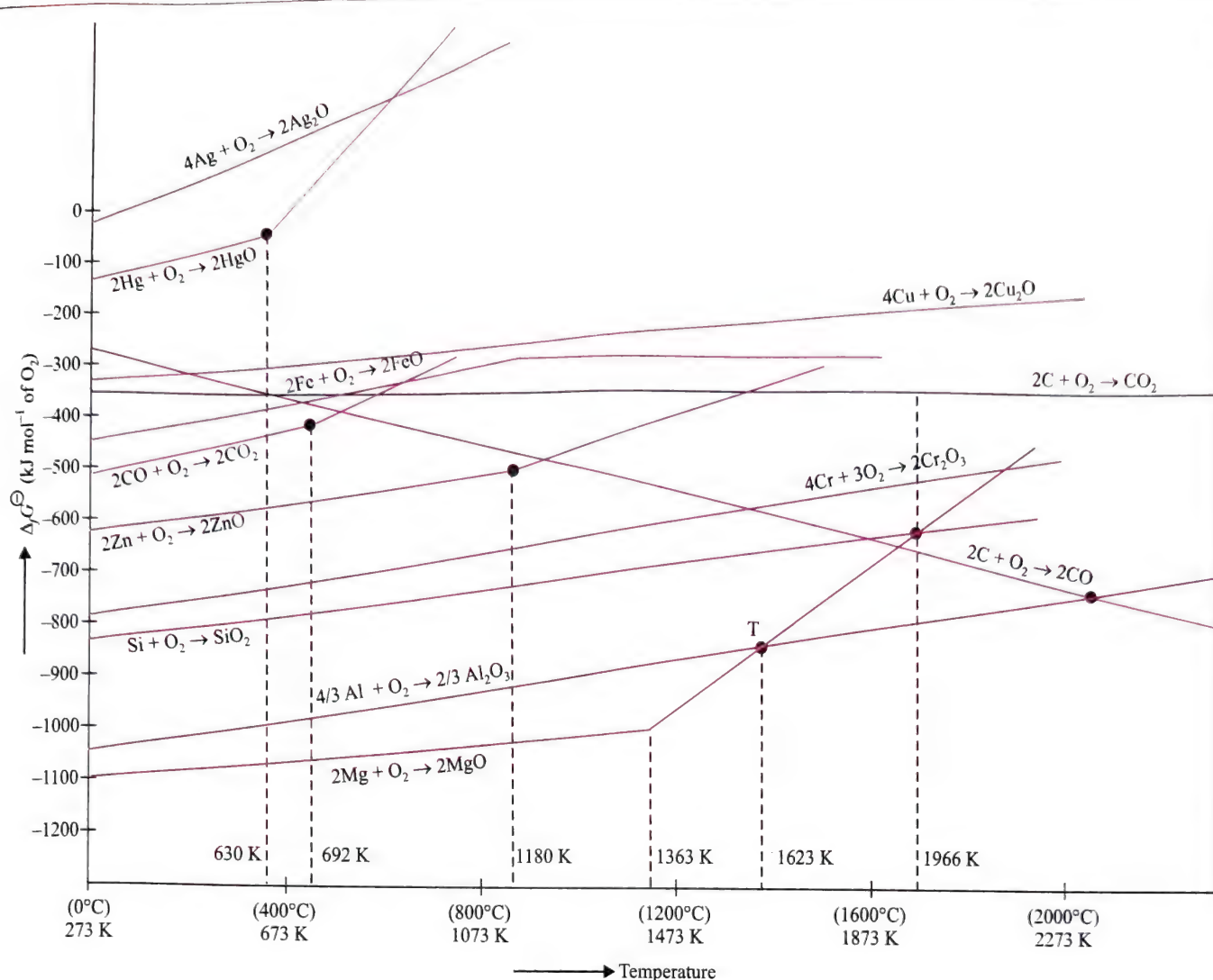


Fig. 1.6 Ellingham diagram for formation of oxides of some elements

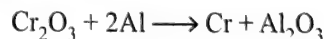
1. The slope of the curves of the formation of metal oxides is +ve as $\Delta_f G^\ominus$ becomes less negative or increases with rise in temperature.
2. Each plot is a straight line except when some change in phase, i.e., solid \rightarrow liquid or liquid \rightarrow gas takes place. The temperature at which such a change occurs is indicated by an increase in the slope on the +ve side. For example, in the Zn–ZnO plot, there is an abrupt increase in +ve slope at 692 K and 1180 K, which indicates the phase change from $\text{Zn}_{(s)} \rightarrow \text{Zn}_{(l)}$, $\text{Zn}_{(l)} \rightarrow \text{Zn}_{(g)}$. Thus 692 K is the melting point and 1180 K is the boiling point of zinc metal.
3. In case of less reactive metals such as Ag and Hg, $\Delta_f G^\ominus$ has more +ve value at high temperatures. This implies that both Ag_2O and HgO are unstable and decompose at high temperatures.

$$2\text{Ag}_2\text{O} \xrightarrow{\Delta} 4\text{Ag} + \text{O}_2$$

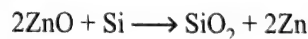
$$2\text{HgO} \xrightarrow{\Delta} 2\text{Hg} + \text{O}_2$$
4. In the plot of CO, $\Delta_f G^\ominus$ decreases as $\Delta_f S^\ominus$ increases, this is indicated by downward trend.
5. Any metal oxide with lower value of $\Delta_f G^\ominus$ is more stable as compared to metal oxide with higher value of $\Delta_f G^\ominus$.

Hence, the metal oxide placed higher in the plot can be reduced by the metal involved in the formation of oxide placed lower in the diagram. For example,

- a. Cr_2O_3 can be reduced by Al metal, but Al_2O_3 cannot be reduced by Cr.



- b. ZnO can be reduced by Si, but SiO_2 cannot be reduced by Zn.



The relative tendency of various elements to act as reducing agent is



1.5.2 LIMITATIONS OF ELLINGHAM DIAGRAM

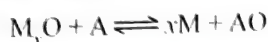
Ellingham diagram simply predicts whether the reduction of a particular oxide with a specific reducing agent is possible or not. Limitations of Ellingham diagram are as follows:

1. **Kinetics of reduction:** It does not tell anything about the kinetics of the reduction reaction, i.e., whether the reduction reaction is slow or fast.

- 2. Reactant/product equilibrium:** The interpretation of $\Delta_f G^\ominus$ is based on the equilibrium constant K .

$$\Delta_f G^\ominus = RT \ln K.$$

Thus, it is assumed that reactants and products are in equilibrium.

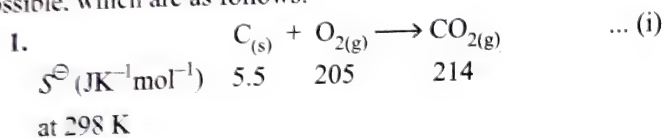


But this is not always true as the reactant/product may be solid.

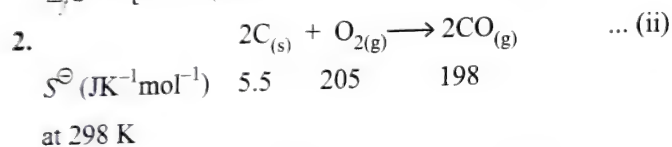
1.5.3 REDUCING NATURE OF CARBON

The process of extracting a metal by reduction of its oxide with carbon (in form of coke, charcoal or carbon monoxide) is called smelting.

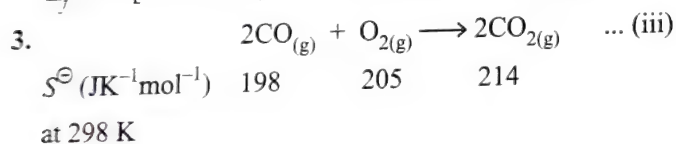
Carbon (graphite) is used as reducing agent, and it forms two different types of oxides, i.e., CO and CO₂. The stability of these oxides varies with the temperature. Three different reactions are possible, which are as follows:



$$\Delta_f S^\ominus = [214 - (205 + 5.5)] = -3.5 JK^{-1}mol^{-1}$$



$$\Delta_f S^\ominus = [2 \times 198 - (2 \times 5.5 + 205)] = 180 JK^{-1}mol^{-1}$$



$$\Delta_f S^\ominus = [2 \times 214 - (2 \times 198 + 205)] = -173 JK^{-1}mol^{-1}$$

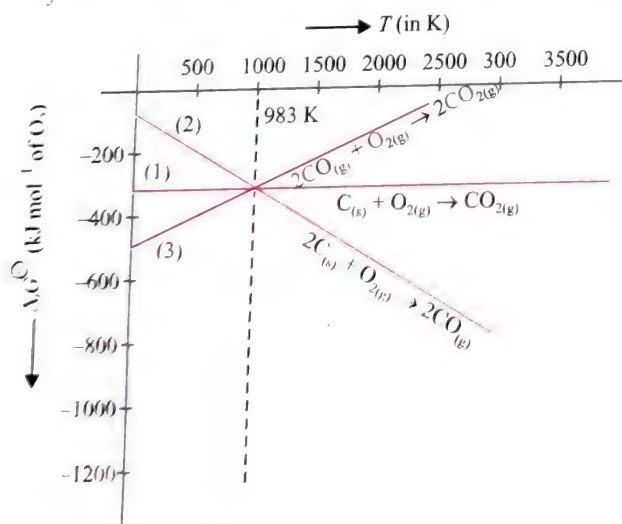


Fig. 1.7 Ellingham diagram for the reducing nature of carbon

- From line (1), it is concluded that C combines with O₂ at all temperatures forming CO₂ and with the increase in temperature, there is hardly any change in $\Delta_f G^\ominus$ value.
- From line (2), it is concluded that as the temperature increases, $\Delta_f G^\ominus$ becomes more and more negative. Likelihood of the reaction to occur increases with temperature.

- From line (3), it is concluded that with the increase in temperature, $\Delta_f G^\ominus$ becomes more and more positive and hence likelihood of the reaction to occur decreases, i.e. CO becomes more stable than CO₂.

- At 983 K, i.e. the temperature at which the three lines intersect, $\Delta_f G^\ominus$ for the forward reaction is equal to $\Delta_f G^\ominus$ for the backward reaction or $\Delta_f G^\ominus$ for the reaction is zero

$$\Delta_f G^\ominus = -2.303 RT \log K = 0$$

where K = equilibrium constant

$$\log K = 0 \text{ or } K = 1$$

- Below 983 K, $\Delta_f G^\ominus (CO_2)$ is more negative than $\Delta_f G^\ominus (CO)$ and hence CO₂ will be formed predominantly. It is further concluded that below 983 K, CO acts as a better reducing agent than C.

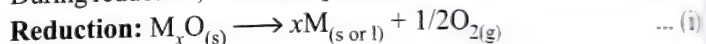
- Above 983 K, $\Delta_f G^\ominus (CO)$ is more negative than $\Delta_f G^\ominus (CO_2)$ and hence CO will be formed predominantly.

Reduction with C at high temperatures is not preferred in all cases due to the following reasons:

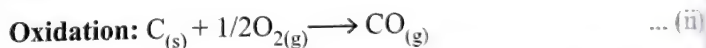
- High cost factor i.e. it is uneconomical.
- Few metals react with C at high temperatures and form carbides.
- Practical difficulties in maintenance of high temperature.

1.5.4 THEORY OF REDUCTION OF METAL OXIDE WITH CARBON

During reduction, the decomposition of the metal oxide takes place.

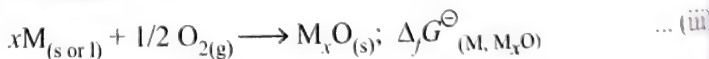


and the reducing agent takes away the oxygen given by the metal oxide.

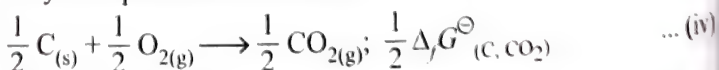


In this case, the role of the reducing agent is to provide a large negative $\Delta_f G^\ominus$ to make the sum of $\Delta_f G^\ominus$ values of the above two reactions (i.e., reduction of the metal oxide and oxidation of the reducing agent) negative.

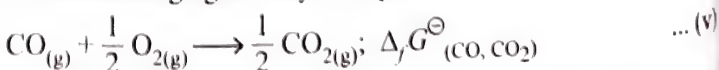
Reversing Eq. (i) one gets equation representing the oxidation of the metal.



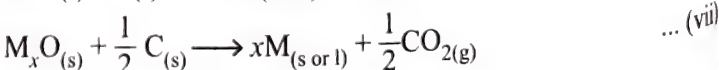
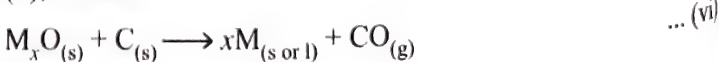
However, instead of partial oxidation of C to CO, if complete oxidation of C to CO₂ occurs, the oxidation of the reducing agent may be represented as follows:



If, instead of C, CO is used as the reducing agent, the oxidation of the reducing agent may be represented as follows:



On subtracting Eq. (iii) from each of the three Eq. (ii), (iv), and (v), we have

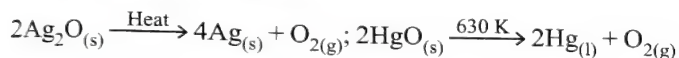




Equations (vi), (vii) and (viii) describe the actual reduction of the metal oxide M_xO to the free metal M . The $\Delta_f G^\ominus$ values for these reactions, in general, can be obtained, by subtraction of the corresponding $\Delta_f G^\ominus$ values from the Ellingham diagram. If these values are -ve, the reduction is feasible, otherwise not.

Alternatively, without going into the calculations for $\Delta_f G^\ominus$ feasibility of a reduction process can be predicted simply by looking at the Ellingham diagram. Metals for which free energy of formation ($\Delta_f G^\ominus$) of their oxides is more negative can reduce those metals for which the free energy of formation ($\Delta_f G^\ominus$) of their respective oxides is less negative. In other words, at any given temperature, any element, (metal) will reduce the oxide of other metals which lie above it in the Ellingham diagram because the free energy change ($\Delta_r G^\ominus$) for the combined redox reaction will be negative by an amount equal to the difference between the free energy of formation ($\Delta_f G^\ominus$) of the two oxides at that temperature. Further, greater the difference, easier is the reduction. For example, Mg can reduce Al_2O_3 , ZnO , FeO and Cu_2O more readily than Al can reduce ZnO , FeO and Cu_2O . Similarly, Al can reduce ZnO , FeO and Cu_2O more readily than Zn reduces FeO and Cu_2O . Thus, the relative tendency of these metals to act as reducing agents is $Mg > Al > Zn > Fe > Cu$.

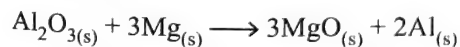
However in case of less reactive metals such as silver and mercury $\Delta_f G^\ominus$ becomes positive at higher temperatures. This suggests that both silver oxide (Ag_2O) and mercury oxide (HgO) are unstable and hence decompose at high temperatures to liberate the corresponding metal.



1.5.5 EFFECT OF TEMPERATURE ON $\Delta_f G^\ominus$ OF THE OVERALL REDUCTION PROCESS

For any process, $\Delta G = \Delta H - T\Delta S$. On increasing the temperature, the values of ΔH and ΔS nearly remain constant, hence the value of $\Delta_f G^\ominus$ becomes more negative. This implies that if a particular reduction process does not occur at a lower temperature, it may occur at a higher temperature. What is required is to select the temperature in such a way that the $\Delta_f G^\ominus$ value of the overall redox reaction becomes negative.

In the Ellingham diagram, this temperature is indicated by the intersection of the two curves, i.e., curve for formation of M_xO and the curve for the oxidation of the reducing agent. At the point of intersection of the two curves, $\Delta_f G^\ominus = 0$. Below this temperature, $\Delta_f G^\ominus$ is -ve and hence the oxide is stable. Above this temperature, $\Delta_f G^\ominus$ is +ve and hence the oxide is unstable, i.e., it would give metal and oxygen. For example, the temperature at the intersection point T of the (Al, Al_2O_3) and (Mg, MgO) curves is approximately 1623 K. Therefore, below 1623 K, MgO is stable and Mg can reduce Al_2O_3 to Al.



But above 1623 K, Al_2O_3 is more stable and hence Al can reduce MgO to Mg.

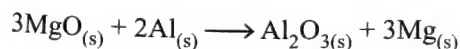
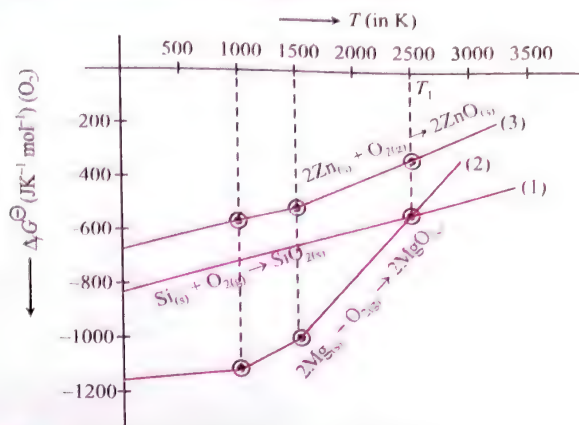
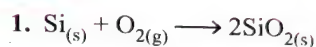


ILLUSTRATION 1.5

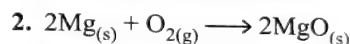
Interpret the following Ellingham diagram.



Sol.



As temperature increases, $\Delta_f G^\ominus$ becomes less negative, hence $\text{SiO}_{2(s)}$ becomes less stable, i.e., at 500 K, SiO_2 is more stable than 2500 K.

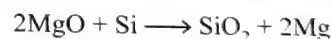


Abrupt changes in the plot at ~800 K and ~1400 K denote phase change/transition from $s \longrightarrow l$ and $l \longrightarrow g$, respectively and represent melting point (~800 K) and boiling point (~1400 K). $\text{MgO}_{(s)}$ becomes less stable with increase in temperature.

At T_1 , lines of (1) and (2) intersect. One can conclude the following:

- At T_1 , both MgO and SiO_2 are equally stable.
- At temperature $> T_1$, MgO is less stable than SiO_2 .

Hence, Si will reduce MgO to Mg.

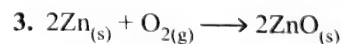


- At temperature $< T_1$, SiO_2 is less stable than MgO .

Hence, Mg will reduce SiO_2 to Si.



Relative stability of MgO and SiO_2 at given temperature can be predicted with the help of Ellingham diagram.



$$\Delta_f G^\ominus (\text{ZnO}) > \Delta_f G^\ominus (\text{MgO})$$

$$\Delta_f G^\ominus (\text{ZnO}) > \Delta_f G^\ominus (\text{SiO}_2)$$

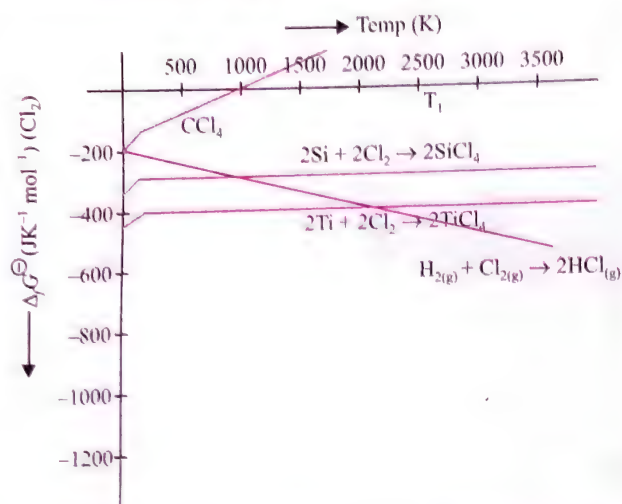
Hence, both $\text{Mg}_{(s)}$ and $\text{Si}_{(s)}$ can be used as reducing agent for reducing $\text{ZnO}_{(s)}$ to $\text{Zn}_{(s)}$.

Important Points:

- Element to be used as reducing agent must form stable oxide than the metal oxide to be reduced.
- The more negative the $\Delta_f G^\ominus$ value for oxide formation at a given temperature, the more difficult it is to reduce the metal oxide concerned.

3. When the plot for one metal is below that for another, the first metal is thermodynamically capable of reducing the oxide of the second.

Reduction of chlorides by C:



The reaction that should take place when C is used for reducing chlorides is



$$\Delta_f G^\ominus(\text{CCl}_{4, g}) < \Delta_f G^\ominus(\text{MCl}, s)$$

Carbon cannot be used as reducing agent to reduce chlorides because $\Delta_f G^\ominus(\text{CCl}_4)$ is less negative than Cl_2 . H_2 can be used above a certain temperature if it is not forming interstitial hydride.

1.5.6 APPLICATION OF ELLINGHAM DIAGRAM IN PYROMETALLURGY

The utility of Ellingham diagrams in pyrometallurgy can be illustrated by considering in detail the extraction of iron, copper, and zinc from their respective oxides.

1.5.6.1 Extraction of Iron from Its Oxides

The chief ores of iron are as follow:

S.No.	Ore	Formula
1.	Haematite	Fe_2O_3 (red oxide of iron)
2.	Magnetite	Fe_3O_4 (magnetic ore of iron)
3.	Limonite	$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (hydrated ore of iron)
4.	Iron pyrites	Fe_2S (also known as fool's gold)
5.	Siderite	FeCO_3 (or spathic ore)

Different forms of iron:

- Cast iron or pig iron:** Impure form and contains 2.5–4% of carbon along with impurities of S, Si, P, and Mn. It is brittle, resistant to corrosion, and is used for sewage pipes.
- Wrought iron or malleable iron:** Purest form and contains minimum amount of carbon (0.12–0.25%), malleable, can be welded, structurally weak, cannot be magnetised, used for making wires, chains, electromagnets, etc.
- Steel:** It contains 0.2–1.5% of carbon; steels containing 0.2–0.5% of C are known as mild steels, while those containing 0.5–1.5% carbon are called hard steel.

Heat treatment of steel: The hardness of steel can be controlled by heat treatment as discussed below:

- Quenching:** Process of heating steel to redness and then sudden cooling by plunging in water or oil. The steel obtained is hard and brittle.
- Annealing:** Process of heating steel to redness and then cooling slowly. Steel obtained is soft.
- Tempering:** Process of heating the quenched steel to a temperature much below redness (200–350°C) and then cooling slowly. Used in making razor blades, axes, knives, swords, etc.
- Case-hardening:** Process of heating wrought iron or mild steel in contact with charcoal and then quenching in oil.
- Nitriding:** Process of heating steels at about 700°C in an atmosphere of ammonia. It gives a hard coating of iron nitride on the surface of steel.

For extraction of iron from its oxide ore, usually **haematite** is used. Process of extraction involves the following steps:

- Concentration:** The ore is crushed in jaw crushers. Crushed ore is concentrated by gravity separation process in which the crushed ore is washed in a stream of water, when lighter sand and clay particles are washed away, while the heavier ore particles settle down. In case of sulphide ore (iron pyrites), concentration is carried out by froth flotation process.
- Calcination:** The concentrated ore is then calcined, i.e., heated strongly in the presence of a limited supply of air in a reverberatory furnace. Following changes are observed:
 - Moisture is removed.
 - Impurities of sulphur, phosphorus, and arsenic escape as their volatile oxides.

$$\text{S}_8 + 8\text{O}_2 \longrightarrow 8\text{SO}_2 \uparrow; \text{P}_4 + 5\text{O}_2 \longrightarrow \text{P}_4\text{O}_{10} \uparrow;$$

$$2\text{As} + 5\text{O}_2 \longrightarrow \text{As}_2\text{O}_5 \uparrow$$
 - Ferrous oxide is oxidised to ferric oxide, thereby preventing the loss of iron as slag during smelting.

$$4\text{FeO}_{(s)} + \text{O}_{2(g)} \longrightarrow 2\text{Fe}_2\text{O}_{3(s)}$$
 - The ore becomes porous and hence is more suitable for reduction to the metallic state. In case of carbonate ore (siderite), during calcination it is converted into ferrous oxide.

$$\text{FeCO}_{3(s)} \longrightarrow \text{FeO}_{(s)} + \text{CO}_{2(g)}$$

$$4\text{FeO}_{(s)} + \text{O}_{2(g)} \longrightarrow 2\text{Fe}_2\text{O}_{3(s)}$$
 However, in case of sulphide ore (iron pyrites), conversion to oxide is carried out by roasting.

$$4\text{FeS}_{2(s)} + 11\text{O}_{2(g)} \longrightarrow 2\text{Fe}_2\text{O}_{3(s)} + 8\text{SO}_{2(g)}$$
- Smelting:** The calcined ore is reduced with carbon i.e. smelted in a blast furnace (Figure 1.8). Blast furnace is a tall cylindrical furnace made of steel and lined inside with fire bricks. It is slightly narrow at the top and again at the bottom. This facilitates the proper flow of materials. The furnace is provided with a double cup and cone arrangement, which helps to feed the charge from the top without letting any gases from inside to escape. Near the top, furnace is

also provided with an outlet for waste gases. At the base, the furnace is provided with

- Small pipes called tuyeres through which a blast of hot air is admitted.
- A tapping hole for withdrawing molten iron.
- A slag hole for withdrawing slag.

The charge consisting of calcined ore (8 parts), coke (4 parts), and limestone (1 part) is introduced into the furnace from the top through cup and cone arrangement. At the same time, a blast of hot air pre-heated to about 1000 K is blown into the furnace through tuyeres. The added coke serves both as a fuel as well as a reducing agent, while added limestone acts as the basic flux.

The temperature near the top of the furnace is ~523 K while near the bottom it is ~2170 K.

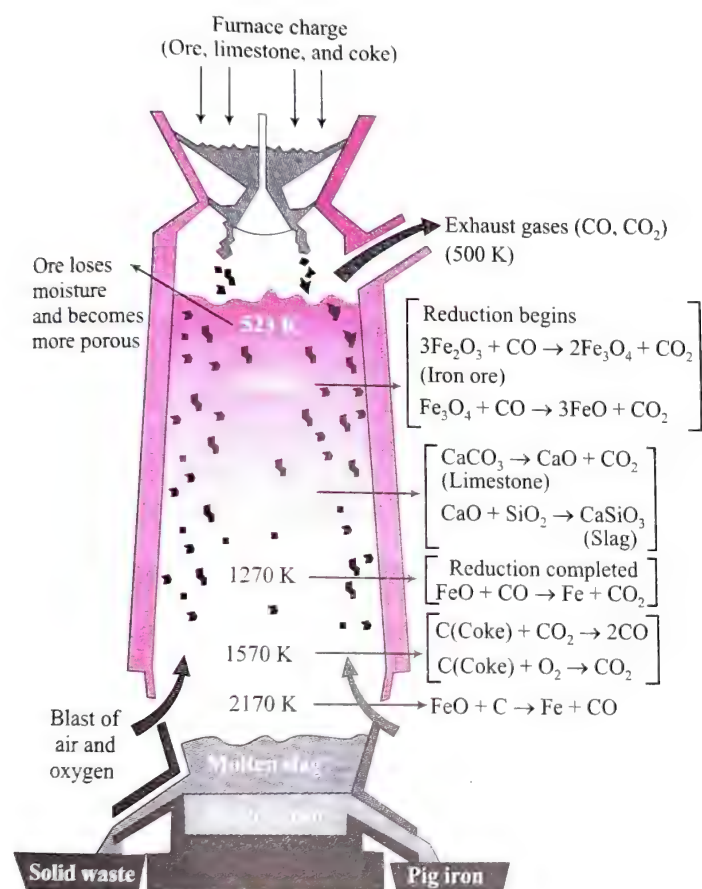
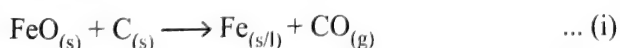


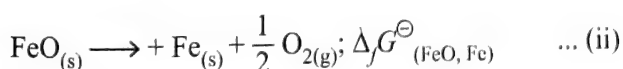
Fig. 1.8 Blast furnace

- a. Theory of reduction process:** Iron oxide is reduced to iron mainly by CO, though perhaps some reduction by C also takes place.

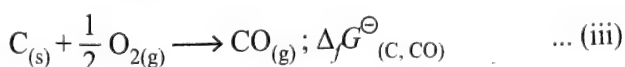


This redox reaction can be divided into the following two half reaction:

i. Reduction:



ii. Oxidation:



The net free energy change of these two combined reactions is



The resultant reaction, i.e., Eq. (i), will take place only when $\Delta_f G^\ominus$ is -ve.

To find the approximate temperature at which this reduction occurs, consider the Ellingham diagram (Figure 1.9).

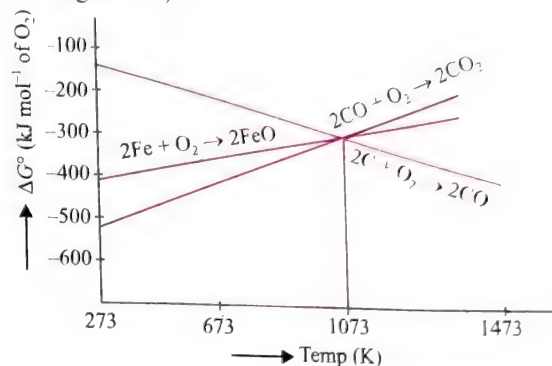


Fig. 1.9 Ellingham diagram for formation of FeO from Fe, CO from C and CO₂ from CO

At approximately 1073 K or above, the (C, CO) line is much below the (Fe, FeO) line. This means, $\Delta_f G^\ominus_{\text{Fe, FeO}} > \Delta_f G^\ominus_{\text{C, CO}}$ and hence $\Delta_f G^\ominus$ is -ve.

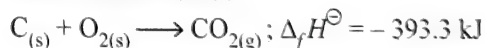
In other words, at 1073 K or above, coke will reduce FeO to Fe and itself will be oxidised to CO.

In contrast, at temperature 1073 K, the (CO, CO₂) line lies below (Fe, FeO) line. Therefore, below 1073 K, CO reduces the oxides of iron, i.e., Fe₂O₃, Fe₃O₄, etc.

Thus, in the blast furnace, reduction of iron oxides takes place at different temperatures. Since the air passes through in a few seconds, the individual reactions do not reach equilibrium.

b. Reactions occurring in the furnace

- i. Zone of combustion:** Near the tuyeres, coke burns to form carbon dioxide.



As the reaction is exothermic, lot of heat is produced and the temperature is ~2170 K.

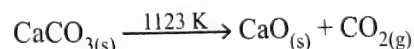
- ii. Zone of heat absorption:** It is the lower part of the furnace and the temperature lies between 1423 and 1673 K. As CO₂ formed near tuyeres moves up, it meets the descending charge. The coke present in the charge reduces CO₂ to CO.

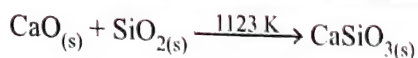


Since this reaction is endothermic, the temperature gradually changes to 1423 K.

- iii. Zone of slag formation:** It is the middle part of the furnace and the temperature is around 1123 K.

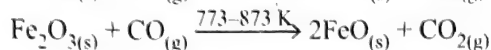
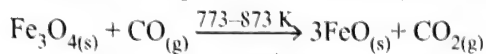
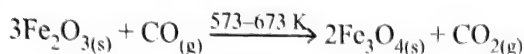
In this zone, limestone decomposes to form CaO and CO₂. The CaO thus formed acts as a flux and combines with silica (present as an impurity) to form fusible calcium silicate slag.



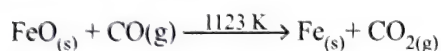


Calcium silicate (slag)

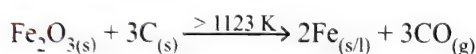
- iv. **Zone of reduction:** It is the upper part of the furnace. The temperature is between 500–900 K. In this zone, the ores are reduced to FeO by CO.



But the further reduction of FeO to Fe by CO occurs around 1123 K.



However, direct reduction of iron ores (i.e., haematite magnetite etc), left unreduced around 873 K, occurs completely to iron by carbon above 1123 K.



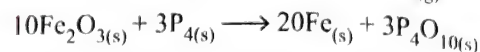
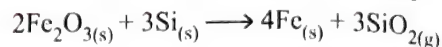
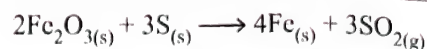
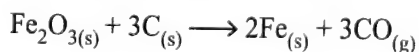
- v. **Zone of fusion:** This is the lower part of the furnace. Temperature here lies between 1423 and 1673 K. In this region, spongy iron melts and dissolves some C, S*, P*, Si*, Mn, etc. CaSiO₃ slag also melts in this region. Both the molten slag and the molten iron trickle down into hearth, where they form two separate layers. The molten CaSiO₃ slag being lighter forms the upper layer, while molten iron being heavier forms the lower layer. The two liquids are periodically tapped off. The iron thus obtained from the furnace contains about 4% carbon and many impurities (e.g., S, P, Si, Mn) in smaller amount. This is called pig iron and is cast into variety of shapes. Cast iron is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

Note: S*, P* and Si* are produced from sulphates, phosphates and silicates, respectively, present in the ore by reduction with carbon.

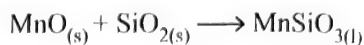
1.5.6.2 Wrought Iron

Wrought iron is the purest form of commercial iron. It contains about 0.2–0.5% carbon besides traces of P and Si in the form of slag. Carbon in wrought iron is present partly as graphite and partly as **cementite** (Fe₃C). Wrought iron is ductile, soft and malleable. The presence of slag in it makes it tough and resistant towards rusting and corrosion. It is, therefore, used to make chains, anchors, bolts, nails and railway carriage couplings. It can be easily magnetised and hence is used to make magnets in electric cranes and dynamos.

1. **Preparation:** Wrought iron is prepared from cast iron by decreasing the carbon content and oxidising the impurities (S, P, Si, Mn, etc.) in a reverberatory furnace lined inside with haematite. The haematite oxidises C to CO, S to SO₂, Si to SiO₂, P to P₄O₁₀ and Mn to MnO.

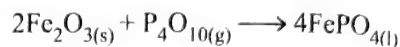


CO and SO₂ thus escape, whereas manganous oxide (MnO) and silica (SiO₂) combine to form slag.



Manganous silicate (slag)

Similarly, phosphorus pentoxide combines with haematite to form ferric phosphate slag:



Ferric phosphate (slag)

Sometimes, limestone is added as a flux, which helps to remove SiO₂ as CaSiO₃ slag. After the reduction, the metal is removed from the furnace and is freed from the slag by passing through rollers.

2. Properties of cast iron:

- It is extremely tough and melts at 1500°C and is highly malleable and ductile.
- Due to presence of 1% slag, it is fibrous and hence can withstand high stresses.
- It softens at about 1000°C, and then it can be forged and welded.
- It can be tempered and magnetised, as it has high magnetic permeability.

3. Use of wrought iron:

- It is used for articles capable of standing high stresses, such as chains, nails, hooks, bolts, etc.
- It is used for making bars and wires.
- It is used for electromagnets and agriculture equipment.

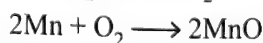
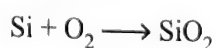
1.5.6.3 Manufacture of Steel

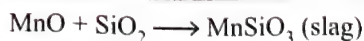
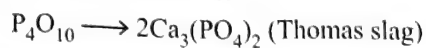
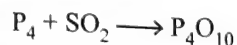
It can be prepared by any of the following processes:

- Bessemer process
- Open hearth process
- LD process

1. **Bessemer process:** This process involves the use of a large egg-or pear-shaped vessel called Bessemer converter. This is made of steel plates lined with silica (SiO₂) or magnesia (MgO) depending upon the nature of impurities present in cast iron. If the impurities are acidic, such as P₄O₁₀ or SO₂, basic lining or lime (CaO) or magnesia (MgO) is used, known as 'basic process'. If impurities are basic such as MnO, lining of silica (SiO₂) bricks is used, known as 'acidic process'. In operation, hot air blast is passed through the molten pig iron. Silicon and manganese (in acidic process) or phosphorous (in basic process) are oxidised to their oxides and are removed as slag.

Acidic process:



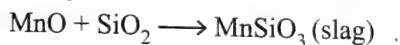
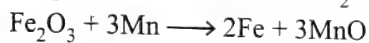
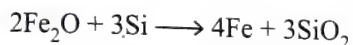
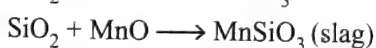
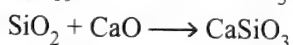
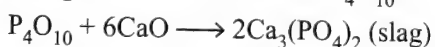
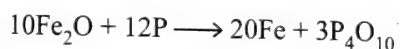
**Basic process:**

Finally oxidation of carbon takes place forming CO, which burns with a blue flame at the mouth of the converter. When no more CO is produced (i.e., flame disappears), a calculated amount of Spiegeleisen (an alloy of Fe, Mn and C) is added and distributed throughout the mass by blowing air some time. Mn and C serve as de-oxidiser and reduce FeO (if any) as the rest dissolves in molten steel. (Mn makes steel harder and increases its tensile strength.)

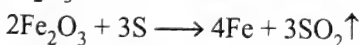
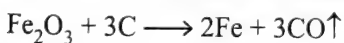
2. Open hearth process: It is a modern process based on the following principles:

- Impurities present in cast iron are oxidised by adding iron ores.
- Percentage of C and Si is brought down by adding scrap iron or low grade wrought iron.
- High temperature is maintained by regenerated system of heat economy.

The charge consisting of cast iron, scrap iron, and haematite is melted in an open hearth furnace. It is lined with lime of magnesia bricks (basic process) for P and S and silica bricks (acidic process) for C, Si, Mn. The furnace is heated by preheated producer gas ($\text{CO} + \text{N}_2$) + a little CO_2 and work on regenerated system.

Acidic process:**Basic process:**

Finally C and S are oxidised forming volatile gases.



Samples of steel are drawn from time to time and tested for their carbon contents. At the appropriate time, ferromanganese or spiegeleisen is added to the molten mass to obtain mild or hard steel, respectively. This process takes 8–10 hr for completion (while Bessemer process takes only 20–30 min). While the molten steel is drawn from the furnace, a little aluminium or ferrosilicon is added to it to remove dissolved gases.

3. LD process: In this process, pure oxygen under a pressure of about 6 to 10 atm is blown through a water-cooled copper tube (called lance) from a distance of 24 inches over the surface of molten cast iron containing up to 18% scarp iron and taken in a converter with basic lining. Impurities of

Si, Mn, P and C are oxidised rapidly and form a slag. The purified metal has a higher density and sinks to the bottom, while its place is taken by impure metal. Thus, convection currents are set up in the converter and the conversion of cast iron into steel is completed in about 45 min. The oxidation reaction being exothermic keeps the whole mass in molten condition.

Properties and uses of steel: Steel combines the use of cast iron and wrought iron. It is hard and elastic. The properties of steel depend upon its carbon content. As percentage C increases, hardness increases but ductility decreases.

- Low carbon or soft steel contains 0.25% C.
- Medium carbon or mild steel contains 0–0.5% C.
- High carbon or hard steel contains 0.5–1.5% C.
- Alloy steel or special steels are alloys of steel with Ni, Cr, Co, Mn, V, W etc.

Alloys of steel:

Alloy	Composition	Properties	Uses
Alnico	Fe-60%, Ni-20%, Al-12%, Co-8%	Highly magnetic	For making permanent magnets
Chrome steel	Cr-2–4%	High tensile strength	For making axles, ball bearing, and cutting tools
Invar	Ni-36%	Low coefficient of expansion	For making watches, metre scales, and pendulum rods
Manganese steel	Mn-13%	Very hard and resistant to wear and tear	For making rock drills, safes, etc.
Nickel steel	Ni-2–4%	Resistant to corrosion, hard and elastic	For making wire cables, gears, and shafts
Stainless steel	Cr-18%, Ni-8%, C-1%	Resists corrosion	For making utensils, cutlery, and ornamental pieces
Tungsten steel	W-5%, C-1%	Retains hardness at high temperature	For making high speed cutting tools

1.5.6.4 Extraction of Copper from Cuprous Oxide [Copper(I) Oxide]

In the Ellingham diagram given in figure 1.10, (Cu , Cu_2O) curve is almost at the top, while the (C , CO) and (CO , CO_2) lines lie much below it particularly in the temperature range 500–600 K. This means that it is very easy to reduce cuprous oxide to metallic copper by heating with coke. But most of the ores of copper are sulphides. Hence, the sulphide ores are first roasted in a reverberatory furnace to convert them into oxides.

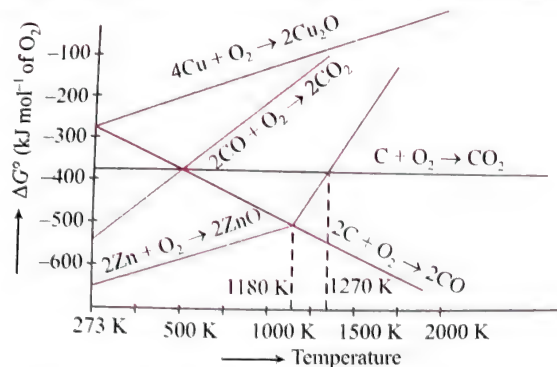
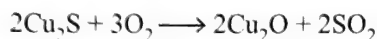
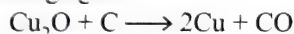


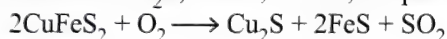
Fig. 1.10 Ellingham diagram showing the formation of Cu_2O from Cu, ZnO from Zn, CO from C, and CO_2 from C and CO



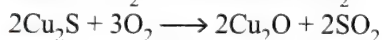
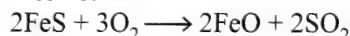
The oxides can then be reduced to metallic copper using coke as the reducing agent.



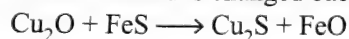
However, in actual process, the sulphide ore (i.e. copper pyrites), after concentration by froth flotation process is roasted in a reverberatory furnace when copper pyrites is converted into a mixture of FeS and Cu_2S , which, in turn, are partially oxidised.



Copper pyrites



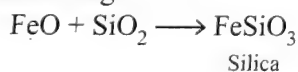
Since iron is more reactive than copper, FeS is preferentially oxidised to FeO than Cu_2S to Cu_2O . If at all any Cu_2O is formed, it combines with FeS and is changed back to Cu_2S .



Thus, the roasted ore mainly contains Cu_2S and FeO along with some unreacted FeS.

The roasted ore is then mixed with silica (flux) and some powdered coke (to check the oxidation of FeO to Fe_2O_3) and heated strongly in a blast furnace. This process is called smelting.

During smelting, FeO combines with silica to form fusible ferrous silicate slag.



At the temperature of the furnace, the entire mass melts and two layers of molten mass are formed. The slag being lighter makes the upper layer, which can be withdrawn from the slag hole from time to time. The lower molten layer is called **copper matte**. It chiefly consists of Cu_2S and some unchanged FeS.

Recovery of copper from matte: The molten matte is transferred to a Bessemer converter, which is a pear-shaped furnace made of steel and lined inside with silica. It is mounted on a horizontal axle and can be tilted in any position. It is fitted with small pipes called tuyeres through which a blast of hot air and fine sand is admitted.

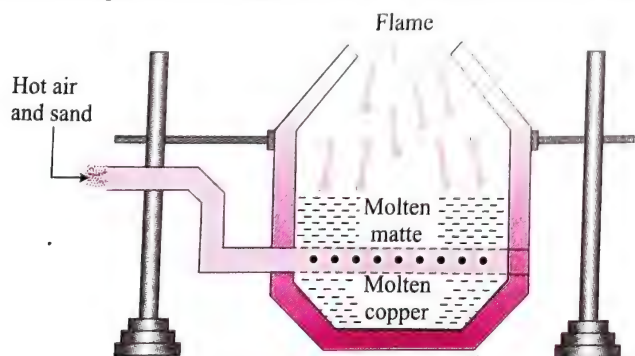
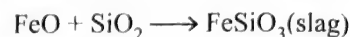
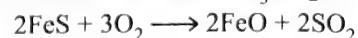
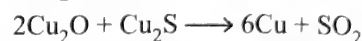


Fig. 1.11 Bessemer converter

During the process of Bessemerisation, any sulphur, arsenic and antimony still present as impurity in matte escape as their respective volatile oxides while FeS is oxidised to FeO, which combines with silica to form FeSiO_3 slag.



The slag thus formed melts and floats on the top of the molten mass and is removed. When whole of iron has been removed as slag, some of the cuprous sulphide undergoes oxidation to form cuprous oxide, which then reacts with cuprous sulphide to form copper metal.



Copper metal so produced falls below tuyeres and thus escapes the oxidising action of the blast. After the completion of the reaction, the converter is tilted and the molten metal is poured in sand moulds. As the metal cools, dissolved SO_2 escapes. Some of the gas bubbles are, however, entrapped during solidification giving blister-like appearance to the metal. The impure metal (containing about 1% impurity) thus obtained is, therefore, called blister copper. Blister copper is finally purified by electrolytic refining as discussed in previous section.

1.5.6.5 Extraction of Zinc from Zinc Oxide

From Ellingham diagram, it is evident that intersection of the (Zn, ZnO) and (C, CO) curves lies at a higher temperature than that of the (Cu, Cu_2O) and (C and CO) curves. Therefore, reduction of ZnO with coke is carried out at a higher temperature than that of Cu_2O .

Further, all the three curves representing the oxidation of carbon [i.e., (C, CO), (C, CO_2) and (CO, CO_2)] lie above the oxidation curve of Zn till the boiling point of zinc (i.e., 1180 K) is reached. Therefore, above 1180 K, $\Delta_f G^\ominus$ for the formation of CO decreases while that for the formation of ZnO increases very rapidly and intersects the (C, CO_2) curve at 1270 K.

In other words, above 170 K, $\Delta_f G^\ominus$ for ZnO is higher than that of CO_2 and CO from carbon. Therefore, above 1270 K, $\Delta_f G^\ominus$ for the reduction of ZnO by carbon is negative and hence ZnO is easily reduced by coke above 1270 K. For the purpose of reduction, ZnO is made into briquettes with coke and clay and heated above 1270 K usually around 1673 K, so that the reduction process essentially goes to completion.

It may, however, be noted here that $\Delta_f G^\ominus$ of CO_2 from CO is always higher than that of ZnO. Therefore, CO cannot be used for reduction of ZnO to Zn.

Since the boiling point of zinc is low (1180 K), the metal is distilled off and collected by rapid chilling.

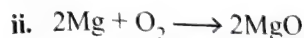
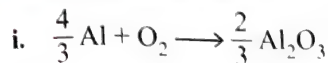
ILLUSTRATION 1.6

- Suggest a condition under which magnesium could reduce alumina.
- Although thermodynamically feasible, in practice magnesium metal is not used for the reduction of alumina in the metallurgy of aluminium. Why?
- Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction?

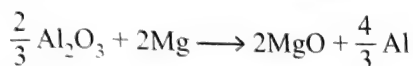
- d. At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps would be more suitable for reducing the leached copper ore and why?

Sol.

a. The two equations are:



All the point of intersection of the Al_2O_3 and MgO curves, $\Delta_r G^\ominus$ becomes zero for the reaction:



Below that point magnesium can reduce alumina.

- b. Temperatures below the point of intersection of Al_2O_3 and MgO curves, magnesium can reduce alumina. But the process will be uneconomical as magnesium is much costlier than alumina.
- c. The entropy is higher if the metal is in liquid state than when it is in solid state. The value of entropy change ($\Delta_r G^\ominus$) of the reduction process is more on positive side when the metal formed is in liquid state and the metal oxide being reduced is in solid state. Thus, the value of $\Delta_r G^\ominus$ becomes more on negative side and the reduction becomes easier.
- d. Zinc being above iron in the electrochemical series (more reactive metal is zinc), the reduction will be faster in case zinc scraps are used. But zinc is costlier metal than iron, so using iron scraps will be advisable and advantageous.

ILLUSTRATION 1.7

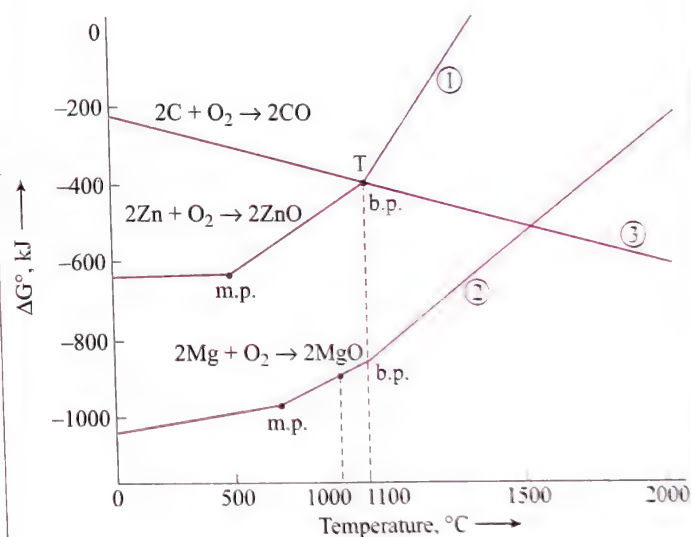
Why is it advantageous to roast a sulphide ore to the oxide before reduction?

Sol. The free energies of formation ($\Delta_f G^\ominus$) of most sulphides are greater than those for CS_2 and H_2S . Carbon disulphide is, in fact, an endothermic compound. So neither carbon nor hydrogen is a suitable reducing agent for metal sulphides. Moreover, the roasting of a sulphide to the oxide is quite advantageous thermodynamically. Hence, the common practice is to roast sulphide ore to the oxide prior to reduction.

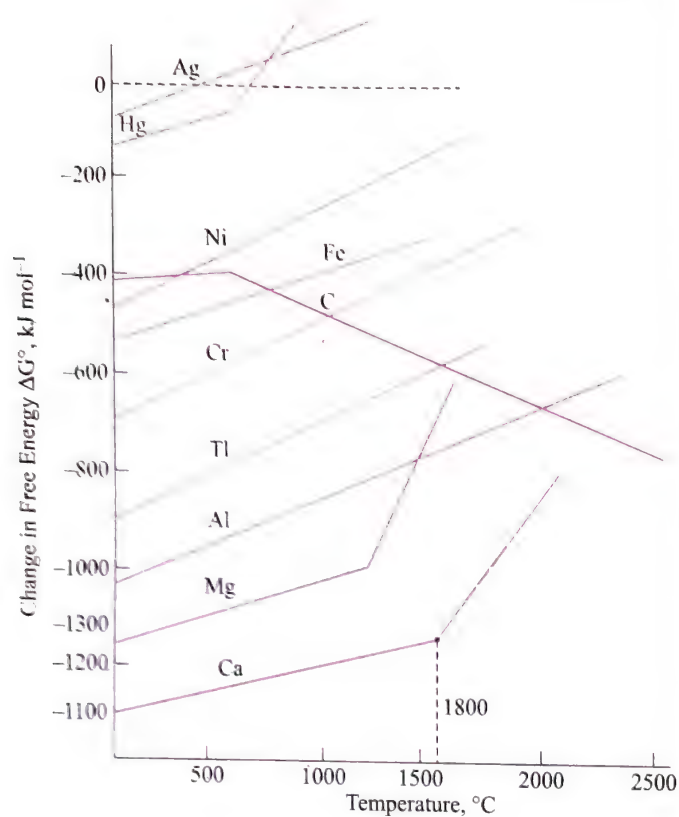
CONCEPT APPLICATION EXERCISE 1.2

- What is the thermodynamic consideration in the choice of a reducing agent in metallurgy?
- Carbon monoxide is more effective reducing agent than carbon below 983 K but above this temperature, the reverse is true. How would you explain this?
- The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with example.

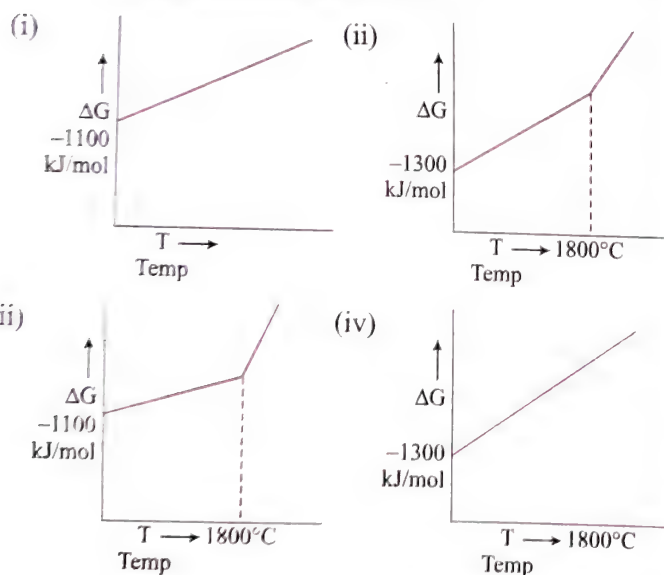
- Which is a better reducing agent at 710°C : C or CO?
- Indicate the temperature at which carbon can be used as a reducing agent for FeO .
- Is it true that under certain conditions, Mg can reduce SiO_2 , and Si can reduce MgO ?
- Which methods would you recommend for the purification of impure metals such as zinc, copper and germanium metals?
- Explain by Ellingham diagram?
 - At temperature above 1073 K, coke can be used to reduce FeO to Fe.
 - CO is more effective reducing agent than C, below 983 K but above this temperature, the reverse is true.
 - Which basic concept is involved in selecting a reducing agent for obtaining metal from its oxide ore?
- The Ellingham diagram for zinc, magnesium and carbon converting into corresponding oxides is shown below:



- What should be the temperature to make the following reduction process spontaneous.
 $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$
 - At what temperature Zn and C have equal affinity for O_2 ?
 - At 1100°C which reaction is spontaneous to a maximum extent.
 - $\text{MgO} + \text{C} \longrightarrow \text{Mg} + \text{CO}$
 - $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$
 - $\text{MgO} + \text{Zn} \longrightarrow \text{Mg} + \text{ZnO}$
 - $\text{ZnO} + \text{Mg} \longrightarrow \text{MgO} + \text{Zn}$
10. Using the following Ellingham diagram answer the following questions:



- (a) Free energy change of Mg and Hg for the conversion to oxides, the slope ΔG vs. T , changes above the boiling of the given metal. Explain.
- (b) Out of Hg, Mg, Fe and Al, which element can be prepared by heating the oxide above 400°C .
- (c) For the conversion of Ca(s) to CaO(s) which of the following represents the ΔG vs. T ?



- (d) Why Al reduces Fe_2O_3 whereas MgO cannot be reduced by Al at 1500°C . Explain.

6. ELECTROCHEMICAL PRINCIPLES OF METALLURGY

As discussed in section 1.5, the principles of thermodynamics are useful in:

1. Selecting a suitable reducing agent for a given metal oxide.

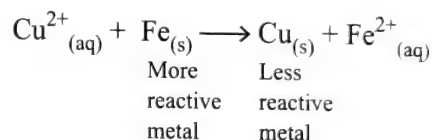
2. Selecting optimum temperature at which reduction reaction proceeds smoothly.

Same principles can also be applied in the reduction of metal ions in solution or molten state. These reductions are usually carried out either by electrolysis or by adding a suitable element as the reducing agent.

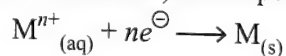
The process of electrolysis has been used to carry out the reduction of molten metal salts. The electrochemical principles of electrolysis can be understood through equation:

$$\Delta G^\ominus = -nFE^\ominus \quad \dots (i)$$

where n is the number of electrons involved in the reduction process, E^\ominus is the standard electrode potential of the redox couple (M/M^{n+}) present in the system. More reactive metals have large negative values of electrode potentials and hence are difficult to reduce. If the difference in E^\ominus values of two redox couples is positive, and consequently ΔG^\ominus in Eq. (i) is negative, then the more reactive metal will displace the less reactive metal from the solution. In other words, less reactive metal will come out of the solution and the more reactive metal will go into the solution. For example,



In simple electrolysis, the ions are discharged at the cathode (negative electrode) and deposited there.



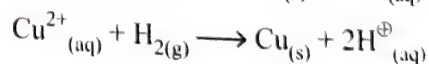
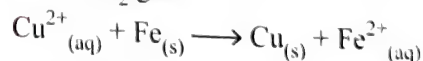
Depending upon the reactivity of the metal produced, the materials of the electrodes are selected. Sometimes, a flux is added for making the molten mass more conducting.

1.6.1 APPLICATIONS OF ELECTROLYSIS TO METALLURGY

The process of extraction of metals by electrolysis of their fused salts is called electrometallurgy. In this process, electrons serve as the reducing agent.

1. Extraction of copper from low grade ores and scraps:

Copper is extracted by hydrometallurgy from low grade ores. The low grade ores are leached by treating with an acid or bacteria when copper metal goes into solution as Cu^{2+} ions. The solution containing Cu^{2+} ions is then treated with scrap iron or H_2 gas.



Since E^\ominus of Fe^{2+}/Fe (-0.44 V) or that of H^+/H_2 (0.0 V) redox couple is lower than that of Cu^{2+}/Cu ($+0.34\text{ V}$), Fe or H_2 can displace Cu from Cu^{2+} ions.

2. Extraction of aluminium from alumina: Fused alumina (Al_2O_3) is a bad conductor of electricity. Therefore, cryolite (Na_3AlF_6) and fluorspar (CaF_2) are added to purified alumina, which not only make alumina a good conductor of electricity but also reduce the melting point of the mix to around 1140 K .

The process of obtaining aluminium by electrolysis of a mixture of purified alumina and cryolite is called **Hall and Heroult process**.

The electrolysis of the molten mass is carried out in an electrolytic cell or tank (Figure 1.12) made of iron using carbon electrodes. The molten electrolyte is covered with a layer of powdered coke to prevent oxidation and loss of heat due to radiation. The temperature of the bath is maintained around 1173 K.

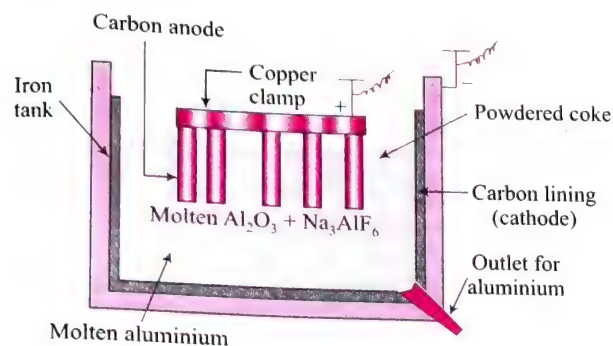
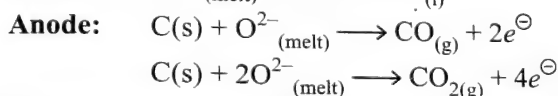
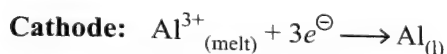


Fig. 1.12 Electrolytic cell for the extraction of aluminium

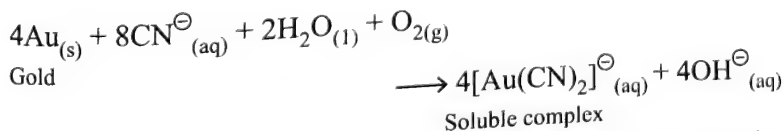
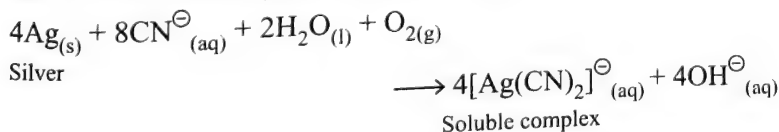
The reactions taking place during the electrolysis are as follows:



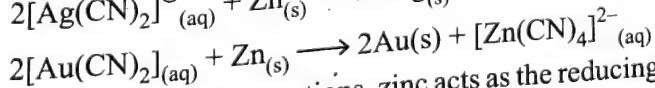
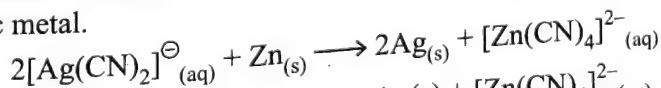
The aluminium metal liberated at the cathode melts at the high temperature (1173 K) of the tank. The molten metal being heavier than the molten electrolyte sinks to the bottom of the tank from where it is withdrawn periodically through the tapping hole. The metal obtained by this process is about 99.95% pure.

1.7 EXTRACTION OF METALS BY BOTH OXIDATION AND REDUCTION

Extraction of gold and silver: We have already discussed in Section 1.4.4.4 that extraction of gold and silver involves leaching of the metals present in the ore with CN^{-} ions. This is also an oxidation reaction because during the leaching process, Ag is oxidised to Ag^{+} and Au to Au^{+} , which then combine with CN^{-} ions to form their respective soluble complexes.



The metals are then recovered from these complexes by reduction or displacement method using a more electropositive zinc metal.



In these displacement reactions, zinc acts as the reducing agent.

Like extraction of copper from low grade copper ores, gold and silver are also extracted from these ores by hydrometallurgy. The process of extraction of metals by dissolving the ore in a suitable reagent followed by precipitation or displacement of the metal by a more reactive or more electropositive metal is called hydrometallurgy.

1.8 REFINING OR PURIFICATION OF METALS

Refining or purification of metals is still required as the metal obtained by any of the processes/methods discussed in the previous sections still has certain impurities present in it and is thus known as **crude metal**.

To obtain metal of high purity, various refining techniques methods are employed depending upon the nature of metal and impurities. Some refining processes are as follows:

1. Distillation
2. Liquation
3. Zone refining
4. Electrolysis
5. Vapour phase refining

These refining processes are discussed in detail in the following sections:

1.8.1 DISTILLATION

Distillation is used for purification of low boiling point or volatile metals, such as mercury (Hg), zinc (Zn), cadmium (Cd) etc. The pure metal is heated and its vapours are separately condensed in a receiver. While the pure metal distills out, impurities (non-volatile) are left behind.

1.8.2 LIQUATION

Liquation is used to concentrate as well as purify metals such as bismuth, tin, lead, mercury, etc, whose melting points are lower than that of the impurities or when the impurity is less fusible than the metal itself.

Impure metal in the form of blocks (ingots) is placed on the sloping hearth (usually of reverberatory furnace). On being heated to a temperature slightly greater than the melting point of pure metal, the metal flows down the hearth, while the impurities (infusible material) are left behind on the hearth (Figure 1.13) charge (impure metal).

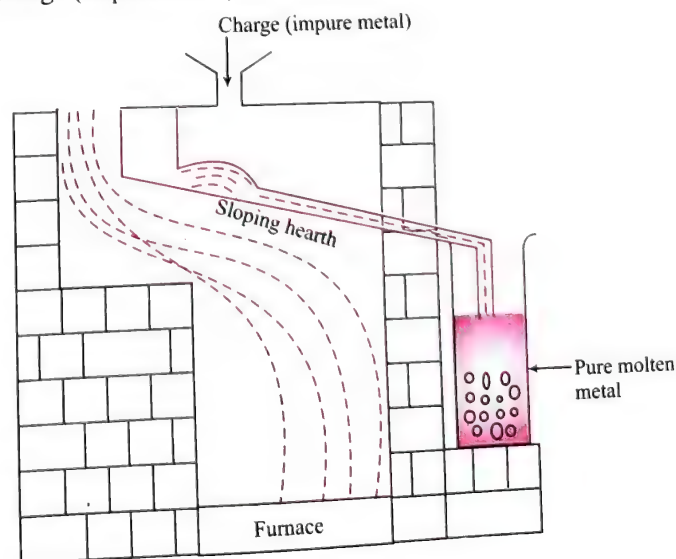


Fig. 1.13 Liquation

1.8.3 ZONE REFINING (FRACTIONAL CRYSTALLISATION)

Zone refining is based on the principle that impurities are more soluble in the melt than in the pure metal (solid). It is used for the purification of germanium, silicon, gallium etc. Metals of high purity can be obtained by removing the impurity, which shows different solubility in the solid and liquid states of the metal. When impure molten metal begins to solidify, the pure metal crystallises, while impurities remain in the melt (liquid).

Impure metal is cast in the form of a rod. This metal rod is enclosed in a tube of inert material. A circular mobile heater is fixed at one end of the rod (enclosed in inert material covering). This whole set-up is enclosed in an inert atmosphere to prevent oxidation of the metal (Figure 1.14). As the heater is moved slowly along the length of the rod, pure metal crystallises out of the melt, whereas the impurities remain suspended in the melt. As the heater is moved, the impurities move along with the heater and get collected at the other end of the rod.

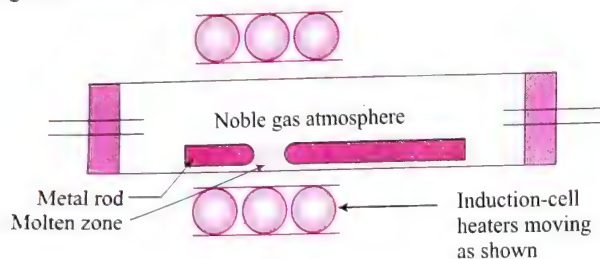


Fig. 1.14 Zone refining

The process is repeated a number of times until the desired state of purity is reached. The end of the rod, where the impurities get collected, is finally chopped off. This method is specially useful for producing semiconductors of very high purity; for example, silicon, germanium purified by this method contain as little as 7–10 ppm of impurities.

1.8.4 ELECTROLYSIS OR ELECTROLYTIC REFINING

Metals such as Cu, Ag, Zn, Sn, Pb, Cr, etc., are refined by electrolysis of aqueous solution of their appropriate salts or a complex of the metal (electrolyte). The blocks of impure metal form the anode, while thin sheet of pure metal acts as cathode. The cathode and anode are suspended in the electrolyte. On passing electric current, at a suitable voltage, metal ions from electrolyte are deposited on the cathode in the form of pure metal, while an equivalent amount of metal dissolves from the anode and goes into the electrolyte solution as metal ions.

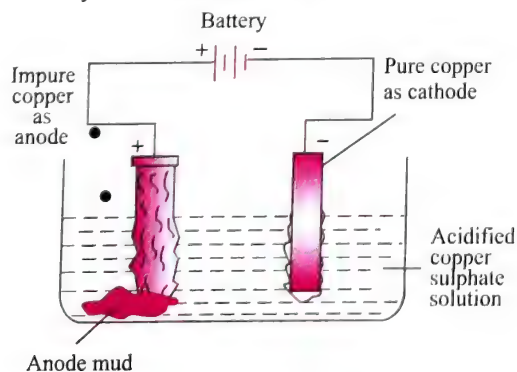
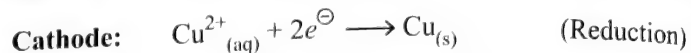
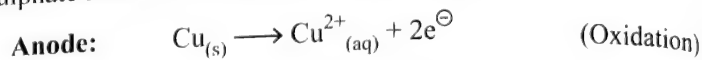


Fig. 1.15 Electrolytic refining of copper

Electrolytic refining results in the transfer of pure metal from the anode to the cathode. The voltage applied for electrolysis is such that the impurities of more electropositive metals remain in

the solution as ions, whereas impurities of the less electropositive metals settle under the anode as anode mud or anode sludge.

For example, in case of Cu refining by electrolysis (Figure 1.15), cathode is the block of impure Cu metal or blister copper, and anode is the thin sheet of pure copper. Electrolyte is copper sulphate solution acidified with sulphuric acid.



The impurities of iron, nickel, zinc, and cobalt present in blister copper being more electropositive pass into solution as soluble sulphates, while the impurities of antimony, selenium, tellurium, silver, gold and platinum being less electropositive are not affected by $\text{CuSO}_4 - \text{H}_2\text{SO}_4$ solution and hence settle down under the anode as anode mud or anode sludge. The recovery of precious metals such as silver, gold and platinum from the anode mud more than compensates for the high cost of electrolytic refining. Copper thus obtained is 99.95–99.99% pure.

1.8.5 VAPOUR PHASE REFINING

Vapour phase refining involves the removal of impurities from the crude metal by:

1. Converting the metal into its volatile compound.
2. Decomposition of the volatile compound to get pure metal.

Hence, the two requirements are:

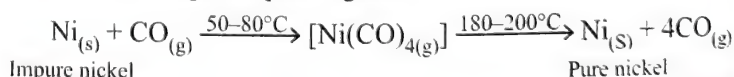
1. Metal should form a volatile compound with suitable reagent.
2. Volatile compound should decompose easily so that the recovery is easy.

This method is exemplified by the following processes.

1.8.5.1 Mond's Process (Thermal Decomposition Method)

It is based on the formation of volatile metal carbonyl, which is then thermally decomposed to get pure metal. It is used for the purification of nickel and iron.

Impure nickel in the form of fine powder is heated in the presence of carbon monoxide at 50–80°C to form volatile nickel carbonyl, $[\text{Ni}(\text{CO})_4]$, which is then passed over the nickel balls maintained at 180–200°C, where it decomposes liberating metallic nickel (which gets deposited on Ni balls) and CO is circulated through the plant again.

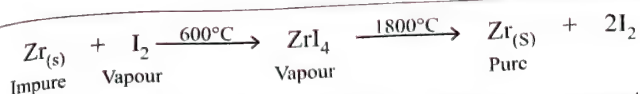


Note: The temperature required for the formation of volatile compound should be less than the temperature required for its decomposition.

1.8.5.2 Van Arkel Method (Filament Growth Method)

It is based on the formation of volatile covalent metal iodide and is used for the purification of those metals which are very difficult to obtain in pure state, e.g. zirconium, titanium, hafnium, vanadium, silicon and beryllium.

Pure, compact zirconium, Zr, was first prepared in 1924 by Van Arkel and De Boer by the reaction between crude zirconium and iodine vapour at 600°C to form volatile zirconium tetraiodide, ZrI_4 .



The vapours of ZrI_4 were allowed to diffuse on a tungsten filament maintained at 1800°C (Figure 1.16). Decomposition of ZrI_4 occurred and pure Zr was deposited on the filament. Iodine liberated is recycled. Pure zirconium can be obtained by drilling out the filament.

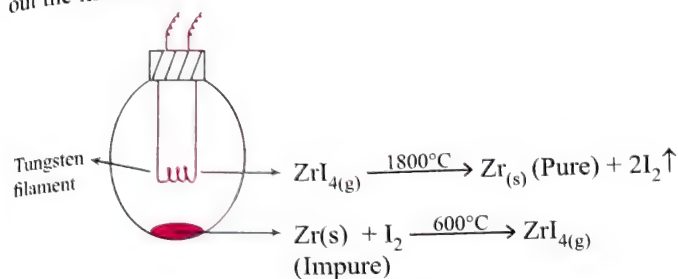


Fig. 1.16 Van Arkel method

Note: Only those metals can be purified by this method whose melting point is greater than 1800°C .

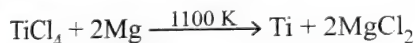
1.8.6 KROLL'S PROCESS

This method is used for purification of those metals for whom neither oxide reduction nor electrolysis is suitable for chemical reasons.

Reduction of metal halide by reactive metals such as magnesium, sodium, calcium is employed.

Titanium is an outstanding example of a metal which cannot be prepared by conventional methods because of its high affinity for oxygen.

In Kroll's process, highly purified TiCl_4 is reduced by magnesium (Mg) in an inert atmosphere (argon).



1.8.7 PARTING'S PROCESS

This process is employed to remove impurity of copper (Cu) and silver (Ag) from gold (Au) by using H_2SO_4 or HNO_3 .

Gold is not attacked by H_2SO_4 or HNO_3 , but copper and silver dissolve in them, when concentration of gold in the sample is less than 30%. If, however, the gold content in the impure sample is more than 30%, then copper and silver are also not attacked by acid of any strength.

Hence, before acid treatment, impure sample is melted with necessary amount of silver to reduce the gold content to ~25% (quartation).

The resulting alloy after being granulated in water is boiled with $\text{H}_2\text{SO}_4/\text{HNO}_3$ when silver and copper passes into solution leaving gold behind. Gold is separated and fused with borax and nitre and 100% gold is obtained. It is cast into ingotes.

1.8.8 VACUUM ARC FURNACE REFINING

Crude metal made into an electrode is progressively melted in an arc furnace under vacuum. As electrode melts, volatile impurities boil off. The molten metal is chilled by pouring into a water-cooled copper crucible. Refractory metals (with high melting point) such as Ti, Zr, Mo are refined by this method.

1.8.9 PYROMETALLURGICAL OXIDATION OR OXIDATIVE REFINING

This method is used when the impurities present in the metal have a greater affinity for O_2 and are more readily oxidised than the metal. This method is usually employed for refining metals such as Pb, Ag, Cu etc. In this method, the molten impure metal is subjected to oxidation by various ways as given below:

1.8.9.1 Furnace Refining or Poling

Air is blown through the molten metal to which a suitable flux may be added. Impurities are oxidised and escape as gases (CO_2 etc.) or pass into the slag. Finally the surface of molten metal is covered with low sulphur coke (to prevent oxidation of the metal), and green logs (poles) of wood are introduced into the molten metal and metal is stirred. Hydrocarbon gases escape from the poles and reduce any oxide of the metal which might have been formed; for example Cu, Sn.

1.8.9.2 Cupellation

In this method, the molten impure metal is heated in a cupel (boat-shaped dish made of bone ash or cement), and a blast of air is passed over the molten metal. The impurities are oxidised, and the volatile oxides thus produced escape with the blast of air. The pure metal remains in the cupel. For example, the impurity of lead present in silver is removed by cupellation.

1.8.9.3 Bessemerisation (Steel Manufacture)

In this method, the impure molten metal is heated in a specially designed furnace and a blast of compressed air is blown through the molten metal. Molten pig iron is purified by this method. The molten pig iron from the blast furnace is taken in a Bessemer converter, and the impurities present in it are oxidised by blast of compressed air.

1.8.10 CHROMATOGRAPHY

It is the most modern and versatile method for separation, purification and testing, the purity of elements and their compounds.

Principle: It is based on the fact that the *different components of a mixture are adsorbed to different extents on an adsorbent*.

Chromatography is essentially a physical technique. It consists of two phases: the stationary phase and the mobile phase. The stationary phase can be either a solid (such as alumina, silica gel) or a tightly bound liquid on a solid support (such as paper in which the liquid water is held by the solid cellulose). On the other hand, mobile phase can be a liquid, gas or a supercritical fluid such as CO_2 . Depending upon the physical state of the stationary phase and the moving phase and also on the process of passage of the moving phase, chromatography can be of several types such as column chromatography, partition chromatography, gas chromatography, etc.

Column chromatography: Column chromatography is one of the simplest chromatographic techniques and is widely used. In column chromatography, an adsorbent such as alumina (Al_2O_3), silica gel or some ion exchange resin is packed in a column (Figure 1.17). This forms the stationary phase. The mixture to be separated is dissolved in a suitable solvent (mobile phase) and applied to the top of the column. Different components of the mixture are adsorbed to different extents depending upon their polarity.

Later the adsorbed components are extracted (eluted) from the column with a suitable solvent (eluent). The component which is more strongly adsorbed on the column takes longer time to travel through the column than a component which is weakly adsorbed. Thus, the various components of the mixture are separated as they travel through the adsorbent (stationary phase).

This technique is especially suitable for such elements which are available only in minute quantities and the impurities are not very much different in chemical properties from the elements to be purified. Lanthanoids (rare earth elements) are purified by this technique using ion exchange as the adsorbent.

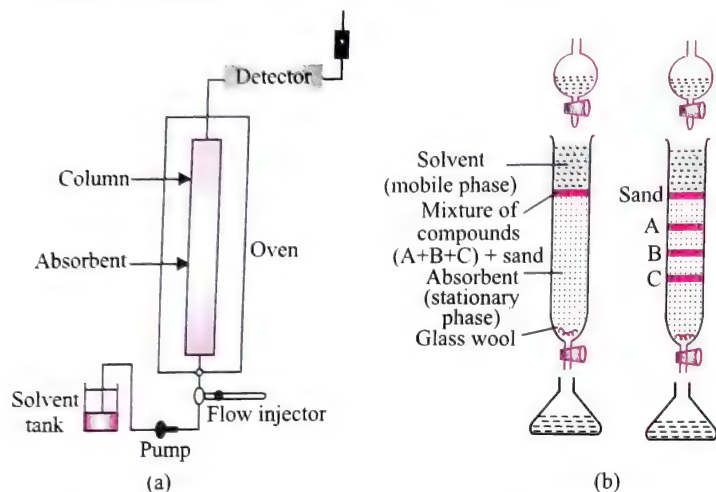
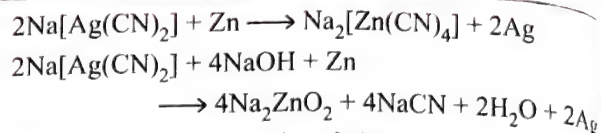


Fig. 1.17 Column chromatography: (a) industrial method and (b) laboratory method

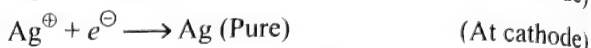


d. Purification (Electrolytic refining)

Electrolyte: AgNO_3 (containing 10% HNO_3) solution

Anode: impure silver

Cathode: thin sheet of pure silver



Impurities like Zn and Cu pass into solution, while gold (if present) falls down as anode mud.

2. Extraction from argentiferous lead

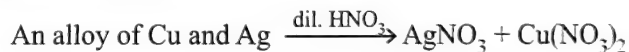
Pb extracted from argentiferous lead contains small quantities of Ag, so it is extracted from it.

a. Parkes process: It is based on the following facts.

- Molten zinc and lead are immiscible; zinc being lighter forms the upper layer.
- Silver is more soluble in molten Zn than molten lead.
- Zn–Ag alloy solidifies earlier than molten lead.
- Zn being volatile can be separated from Ag by distillation.

b. Pattinson's process: Argentiferous lead is melted and cooled when at first lead gets solidified and thus removed. Entire process is repeated many times till entire mass solidifies. At this stage, Pb–Ag alloy containing nearly 2–4% Ag is obtained, which is recovered by cupellation.

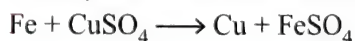
3. Recovery of Ag and Cu from its alloy:



- $\text{AgNO}_3 + \text{Cu(NO}_3)_2 \xrightarrow[250^\circ\text{C}]{\Delta} \text{AgNO}_3 + \text{CuO} + 2\text{NO}_2 \uparrow$
- AgNO_3 and CuO are washed in water. CuO is obtained as residue and the filtrate contains AgNO_3 . The filtrate is heated very strongly to give silver (Ag).



- The residue is dissolved in dil. H_2SO_4 to obtain CuSO_4 . CuSO_4 is treated with scrap iron to get Cu.



1.10 EXTRACTION OF GOLD (Au)

A few commercially important sources of gold are as follows:

S.No.	Ore	Formula
1.	Alluvial sand	Native state, Au (gravel)
2.	Calaverite	AuTe_2
3.	Sylvanite	AuAgTe_2

Extraction of gold depends upon the nature of the ore.

1. Extraction of vein gold: Amalgamation process is employed for extraction of gold from hard auriferous quartz rocks. It involves the following two steps:

1.9 EXTRACTION OF SILVER (Ag)

A few commercially important ore of Ag are as follows:

S.No.	Ore	Formula
1.	Horn silver	AgCl (chiorargyrite)
2.	Argentite	Ag_2S (silver glance)
3.	Ruby silver	$3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$
4.	Proustite	Ag_3AsS_3
5.	Stromeyerite	$\text{Ag}_2\text{S} \cdot \text{Cu}_2\text{S}$ (silver copper glance)

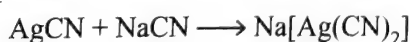
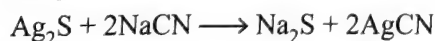
} Principal ores of Ag

Extraction of silver (Ag):

1. Extraction from silver ores (cyanide process)

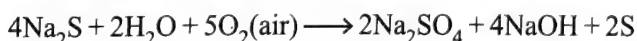
a. Crushing and concentration: The powdered ore is concentrated by froth flotation method.

b. Treatment with NaCN (leaching): The concentrated ore is leached with NaCN solution (0.5%) in presence of air when silver and its salt are converted to soluble complex.



Sodium dicyanoargentate(I) (soluble)

Oxygen in air converts Na_2S to Na_2SO_4 and hence reversibility of reaction is checked.



c. Precipitation of silver: It is done by adding Zn dust (Zn being more electropositive than Ag).

- a. **Crushing and milling:** The gold-bearing rocks are broken into small pieces by rock crushers and then powdered by means of a battery of stamp mills working in series. Each stamp mill consists of a huge pestle (stamp) and a mortar (die) made up of steel. Each stamp weighs about 1250 lbs and falls through a height of 7.5 inches over the crushed rock on the mortar at the rate of 100 strokes per minute. The stamps are raised by rotating camshaft and then dropped by gravity. The powdered ore is washed out of the stamp mill through the screen by the current of water. The screen allows only fine particles to pass, while bigger particles are retained, which are powdered again.
- b. **Amalgamation:** The slurry flowing out of the stamp mill is then passed over amalgamated copper plates placed just in front of the stamp mills. The heavier gold particles are retained by mercury to form gold amalgam. The gold amalgam is scrapped off from time to time and distilled in iron retorts when mercury distils over leaving behind pure gold.
2. **Extraction from gold ores:** MacArthur–Forest cyanide process is used for the extraction of gold from the sulphide or telluride ore, which involves the following steps:
- a. **Crushing, grinding, and concentration:** The gold ore is crushed and powdered and then concentrated by froth flotation process.
- b. **Roasting:** The concentrated ore is roasted in excess of air or oxygen when impurities of sulphur, arsenic, and tellurium are oxidised and escape as their volatile oxides.
- c. **Treatment with KCN:** The finely powdered roasted ore is taken in large vats made up of cement or iron and having false wooden bottoms with holes. It is then treated with a dilute (0.5%) solution of KCN in presence of excess of air for 24 hrs. As a result, gold dissolves in KCN to form a soluble complex called potassium dicyanidoaurate(I).
- $$4\text{Au} + 8\text{KCN} + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{K}[\text{Au}(\text{CN})_2] + 4\text{KOH}$$
- Potassium
dicyanidoaurate(I)
- d. **Precipitation of gold:** The above solution containing potassium dicyanidoaurate(I) is filtered to remove insoluble impurities and then treated with zinc dust, when gold being less electropositive than zinc gets precipitated.
- $$2\text{K}[\text{Au}(\text{CN})_2] + \text{Zn} \longrightarrow \text{K}_2[\text{Zn}(\text{CN})_4] + 2\text{Au} \downarrow$$
- The precipitated gold is recovered by filtration.
3. **Refining of gold:** Gold obtained by any of the above methods is impure and contains silver, copper, zinc and sometimes lead as impurities. These impurities are removed as follows:
- a. **Cupellation:** The impure metal is melted in a cupel in presence of borax and silica and air is passed through the fused mass. Zinc and lead are oxidised and are blown off while silver and a small amount of Cu remains, which are then removed by the parting process.
- b. **Parting process:** Removal of impurities of silver and copper from gold is called parting. It is carried out by boiling impure gold with either conc. H_2SO_4 or conc. HNO_3 when copper and silver dissolve while gold remains unaffected.
- $$\text{Cu} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$$
- $$2\text{Ag} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Ag}_2\text{SO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$$
- It is, however, found that if the percentage of gold in the impure sample is more than 30%, the sample is not attacked by the acid. More silver is, therefore, added to the sample till an alloy containing about 25% of gold is obtained. This is then treated with boiling conc. H_2SO_4 when Ag and Cu dissolve leaving behind gold.
- c. **Miller's process (chlorine parting):** Parting with chlorine is sometimes used. Impure gold is fused, covered with borax, and dry chlorine gas is passed through it. Gold is unaffected (gold chloride being unstable at high temperatures), while the other metals form chlorides. Silver chloride floats on the surface, whereas the chlorides of other metals (such as Hg, Zn, As etc.) are volatilised. The silver chloride is skimmed off leaving behind only gold.
- d. **Electrolytic refining:** This method is used when very pure gold is required. The impure gold is made the anode, while a thin sheet of pure gold acts as the cathode. The electrolyte consists of a solution of auric chloride (AuCl_3) acidified with 10–12% HCl . On passing current of high density, pure gold gets deposited on the cathode.

1.11 EXTRACTION OF ZINC (Zn)

A few commercially important ores of zinc are as follows:

S.No.	Ore	Formula
1.	Zinc blende	ZnS
2.	Zincite	ZnO (red oxide)
3.	Zinc spine	ZnAlO_2
4.	Calamine	ZnCO_3
5.	Willemite	Zn_2SiO_4 ($\text{ZnSiO}_3 \cdot \text{ZnO}$)

Extraction of zinc:

1. **Concentration:** The ore is concentrated first by gravity method and then by froth flotation process. If Fe_2O_3 is present as an impurity, it is removed by magnetic separation.
2. **Roasting:** The concentrated ore is then roasted at $900^\circ\text{--}1000^\circ\text{C}$ to convert ZnS and ZnSO_4 to ZnO .
- $$2\text{ZnS} + 3\text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{SO}_2$$
- $$\text{ZnS} + 2\text{O}_2 \longrightarrow \text{ZnSO}_4$$
- $$\text{ZnSO}_4 \longrightarrow 2\text{ZrO} + 2\text{SO}_2 + \text{O}_2$$

Note: If calamine is used as the source, only calcination is required at high temperature. $\text{ZnCO}_3 \longrightarrow \text{ZnO} + \text{CO}_2$

- 3. Reduction of coke:** The oxide ZnO is reduced with coke at about 1500°C to obtain metallic zinc.



- 4. Electrolytic refining:** Zn thus produced contains impurities like Pb, Cd and Fe. These impurities are removed by liquation. Pure zinc is obtained by electrolysis of zinc in presence of acidified ZnSO_4 ($\text{ZnSO}_4 + \text{dil. H}_2\text{SO}_4$) as electrolyte. Impure zinc is made the anode and pure zinc, the cathode.

Note: Zinc can also be extracted by electrolytic method. ZnS is first roasted at 700°C to produce ZnO. Then, the oxide ZnO is leached with H_2SO_4 to convert to sulphate (ZnSO_4). After removing impurities by treating with milk of lime, ZnSO_4 is acidified and electrolysed to give pure zinc on cathode.

1.12 EXTRACTION OF ALUMINIUM (Al)

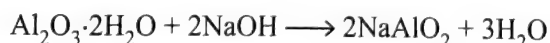
A few commercially important ores of aluminium are as follows:

S.No.	Ore	Formula
1.	Bauxite	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (principal ore)
2.	Corundum	Al_2O_3
3.	Feldspar	KAlSi_3O_8 or $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$
4.	Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$
5.	Diaspore	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
6.	Cryolite	Na_3AlF_6
7.	Clay	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ (kaolin)

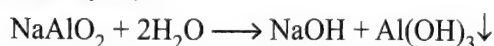
Extraction of aluminium: Electrolytic method from bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$)

- 1. Purification of bauxite:** Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) contains mainly Iron oxide and silica as impurity. It is difficult to remove iron or silicon from aluminium, so the ore is purified before hand. It can be achieved by either of the following processes.

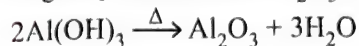
- a. Bayer's process (for ores containing iron oxide as major impurity):** Finely grounded ore is roasted at a low temperature to convert FeO to Fe_2O_3 and digested with a concentrated solution of NaOH in an autoclave. Al_2O_3 (amphoteric) dissolves forming NaAlO_2 , while Fe_2O_3 (basic) remains undissolved. Fe_2O_3 is removed by filtration.



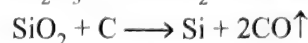
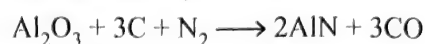
The filtrate containing sodium aluminate is diluted, treated with a seed crystal of pure $\text{Al}(\text{OH})_3$, and then agitated, when pure $\text{Al}(\text{OH})_3$ is precipitated (by slow hydrolysis).



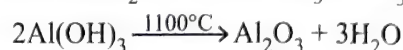
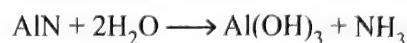
The precipitated $\text{Al}(\text{OH})_3$ is filtered, washed and ignited to give pure alumina (Al_2O_3).



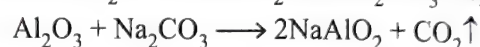
- b. Serpek's process (for ores containing silica, SiO_2):** The powdered ore is mixed with carbon and heated to 1800°C in a current of nitrogen, where aluminium nitride is formed. SiO_2 is reduced to silicon, which volatilises away.



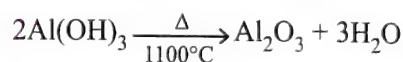
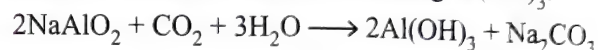
Aluminium nitride is hydrolysed by water to $\text{Al}(\text{OH})_3$, which on ignition gives pure alumina.



- c. Hall's process:** Crude bauxite reacts with Na_2CO_3 at 1000°C to give sodium aluminate, and impurities Fe_2O_3 and SiO_2 form NaFeO_2 and Na_2SiO_3 respectively.

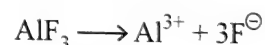


CO_2 at a temperature of around 60°C is passed into sodium aluminate solution producing $\text{Al}(\text{OH})_3$.

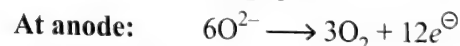
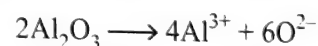


- 2. Electrolytic reduction of alumina:** Aluminium cannot be isolated by electrolysis of aqueous solution of Al_2O_3 . Since aluminium is more electropositive than hydrogen, so its electrolysis gives H_2 at cathode.

Al_2O_3 is infusible (MP = 2050°C), so it cannot be electrolysed. So pure alumina dissolved in molten cryolite (Na_3AlF_6) containing some CaF_2 or NaF is electrolysed at about $800\text{--}1000^\circ\text{C}$. The electrolysis is carried out in an iron cell lined with graphite (cathode). The anode is a series of graphite rods.



At the same time, Al_2O_3 dissociates into Al^{3+} and O^{2-} . Since 'O' is below F in the electronegativity series, O^{2-} ions are selectively discharged at the anode as oxygen.



The oxygen liberated at the anode combines with the carbon of the anode to form CO and CO_2 , so the anode, which burns away, has to be replaced periodically. Molten Al collects at the bottom of cell (99% pure).

- 3. Electrolytic refining:** The cell layers contain three fused layers:

- The bottom anode layer of an alloy of Al, Cu, Si
- The middle layer of cryolite and BaF_2
- The top cathode layer of pure aluminium.

When a current is passed, Al^{3+} ions from the fused middle layer get discharged at the cathode, while an equivalent

amount of aluminium moves into the middle layer. Impurities (Cu etc.) remain at the bottom.

1.13 USES OF ALUMINIUM, COPPER, ZINC AND IRON

1.13.1 USES OF ALUMINIUM

1. Aluminium foils are used for wrapping fine articles like photographic films, pharmaceutical products, cigarettes, chocolates, sweets, etc.
2. Aluminium powder, being highly reactive, is used as a reducing agent in aluminothermic process for the extraction of chromium and manganese from their oxides.
3. Aluminium is a cheap metal which resists corrosion. Therefore, it is used for making household utensils, cans for drinks, tubes for toothpaste, picture frames, trays, etc. It is used in buildings for making angles for doors, windows, etc.
4. Fine dust of aluminium is used for making aluminium paints and lacquers. For example, aluminium powder mixed with linseed oil shines like silver and is called **silver paint**.
5. Being light and good conductor of electricity (on weight to weight basis, Al conducts twice as Cu), aluminium is used for making transmission cables and for winding the moving coils of dynamos or motors.
6. Aluminium powder is used for flashlight bulbs in indoor photography.
7. Alloys of aluminium, being light, are very useful as listed below:

S. No.	Alloy	Composition	Important properties	Uses
1.	Aluminium bronze	Al = 95%, Cu = 5%	Light strong alloy with golden lustre, resistant to corrosion	Coins, utensils, jewellery, picture frames, etc.
2.	Magnalium	Al = 95%, Mg = 5%	Light, tough, and strong	Light instruments, balance beams, pressure cookers, etc.
3.	Duralumin	Al = 95%, Cu = 4%, Mg = 0.5%, Mn = 0.5%	Light, tough, ductile, resistant to corrosive action	Making aeroplanes, automobile parts, pressure cookers, etc.

1.13.2 USES OF COPPER

1. Copper being a good conductor of electricity is extensively used for making electric cables and other electrical appliances.
2. Copper being a good conductor of heat is used for making utensils, steam pipes, kettles, evaporating pans, calorimeters, etc.
3. Manufacture of copper sulphate.

4. Electroplating and electrotyping.
5. Manufacture of phthalocyanine dyes and pigments.
6. Some important alloys of Cu with their uses are mentioned below.

S. No.	Alloy	Composition	Uses
1.	Brass	Cu = 60–80%, Zn = 40–20%	For castings, condenser tubes, utensils etc.
2.	Bronze	Cu = 75–90%, Sn = 10–25%	For coins, bells, statues etc.
3.	Aluminium bronze	Cu = 90%, Al = 10%	For picture frames, golden powder for pairs.
4.	Bell metal	Cu = 80%, Sn = 20%	For bells and gongs
5.	Monel metal	Cu = 30%, Ni = 67%, Fe and Mn = 3%	For acid pumps and acid containers
6.	German silver	Cu = 25–50%, Zn = 25–35%, Ni = 10–35%	For ornaments, resistant wire
7.	Gun metal	Cu = 88%, Sn = 10%, Zn = 2%	For gears, gun barrels

1.13.3 USES OF ZINC

1. It is used for protecting iron sheets from corrosion or rusting. This process is known as galvanisation.
2. Zinc plates and rods are used in batteries and dry cells.
3. It is used in laboratory preparation of H_2 gas.
4. Zn dust is used as a reducing agent in the manufacture of dye stuffs, paints, extraction of gold and silver by the cyanide process etc.
5. It is used in the preparation of paints like lithopone.
6. Some useful alloys of Zn are as follows

S. No.	Alloy	Composition	Uses
1.	Brass	Cu = 80%, Zn = 20%	For making utensils, wires, castings, condenser tubes.
2.	German silver	Cu = 55%, Zn = 25%, Ni = 20%	For making coins, cooking utensils, statues, etc.
3.	Die casting metal	Zn = 92.5%, Al = 4%, Cu = 3.5%	

1.13.4 USES OF IRON

1. Cast iron, which is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes, toys, etc.
2. It is used in the manufacture of wrought iron and steel.
 - a. Wrought iron, being tough and resistant to rusting, is used for making anchors, wires, bolts, nails, railway carriage couplings, and agricultural implements.

- b. Steel finds a number of uses. Alloy steel is obtained when other metals are added to it. Some alloy steels and their composition, properties, and uses are listed below:

S. No.	Alloy	Composition	Properties	Uses
1.	Stainless steel	Fe = 73%, Cr = 18%, Ni = 8% and carbon 1%	Resists corrosion	For making utensils, cutlery, cycles, automobiles, pens, etc.
2.	Nickel steel	Fe = 96–98%, Ni = 2–4%	Resistant to corrosion, hard and elastic	For making cables, automobiles and aeroplane parts.
3.	Chrome steel	Fe = 96–98%, Cr = 2–4%	High tensile strength	For making axles, ball bearings, cutting tools and crushing machines.
4.	Invar	Fe = 64%, Ni = 36%	Practically no coefficient of expansion	For making watches, meter scales, pendulum rods, etc.
5.	Alnico	Fe = 60%, Al = 12%, Ni = 20%, Co = 8%	Highly magnetic	For making permanent magnets

1.14 FURNACE

Furnace is a device in which high temperature is produced either by burning a fuel or by using electricity. Several types of furnaces are used in the extraction of metals. The important ones are described as follows:

1.14.1 REVERBERATORY FURNACE

This is a kind of furnace (Figure 1.18) in which fuel does not come in direct contact with the charge. The flames are deflected from the roof of the furnace to the charge undergoing reaction. Thus, this furnace can be used for reduction as well as oxidation.

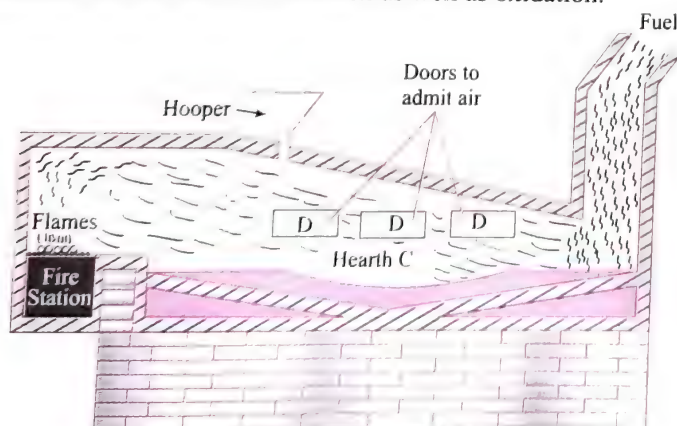


Fig. 1.18 Reverberatory furnace

The furnace consists of three main parts, namely, **fire place**, **hearth** and **chimney**. The fire place is built at one end of the furnace at slightly lower level than that of the hearth. The roof is made slanting and connects with the chimney on the other end. The hot gases from the fire place are reflected by the concave

ceiling over the hearth. The furnace is surrounded on all sides by walls of fire bricks. Air supply can be controlled by vents and direct blast.

The furnace is used for smelting (reduction) and roasting of the ores. The reduction is done by the use of some suitable reducing agent. The furnace is used (a) for reducing the roasted tin stone (SnO_2) to molten tin metal by the use of coke, (b) for roasting the galena ore (PbS) as to convert it into PbO and PbSO_4 by the use of air and (c) for roasting of copper pyrites (CuFeS_2) as to convert it into Cu_2O and FeO by means of air.

1.14.2 MUFFLE FURNACE

Muffle furnace (Figure 1.19) is used when high temperature is required and the fuel and its products of combustion are not to be desired to come into contact with the material to be heated. The muffle is a chamber made of refractory material. The muffle is surrounded by hot flames and hot gases all around. In an electric muffle furnace, the closed chamber is surrounded by heating electric coils. Such a furnace is used for the extraction of zinc and for annealing of gold and silver assaying.

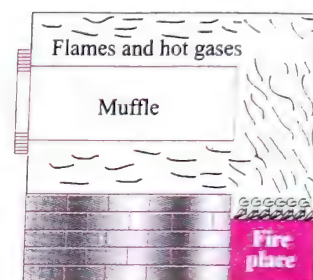


Fig. 1.19 Muffle furnace

1.14.3 ELECTRIC FURNACE

In these furnaces, electrical energy is converted into heat energy. Such furnaces are largely used where cheap power is available and very high temperatures are required and also for carrying electrolytic reduction. The electric furnaces are generally of three types:

1. Induction furnace
2. Arc furnace
3. Resistance furnace

1. Induction furnace: In this furnace, the charge lying on the furnace bed or in a crucible constitutes the secondary coil of an induction unit, and the induced currents produced by making and breaking the primary circuit heat up the material.

2. Arc furnace: Heat is generated by arcs and a temperature over 3000°C may be obtained. Carbon electrodes are used to carry the current and an arc is struck between them and the charge. Arc furnaces are of two types:

- a. Direct heat
- b. Indirect heat

In direct heat arc furnace, arc is used to heat up a gas in which the arc is burning, and in indirect heat arc furnace, the arc burns above the charge, i.e., the arc radiates heat towards the charge.

3. Resistance furnace: Heat is generated by the resistance in the electric circuit. In some cases the material forming the charge may act as the resistance, and in other cases the body of furnace is made up of resistance material and

this material cause heating. In some cases, rods of poorly conducting materials are embedded into the charge, which becomes intensely hot on passage of current.

1.15 REFRACTORY MATERIALS

The materials which can withstand very high temperatures without melting or becoming soft are known as refractory materials. These are not affected by slags formed during the extraction of metals. These are used in the form of bricks for the internal linings of furnaces. Refractory materials used are of three types:

1. **Acid refractories:** Silica, quartz, siliceous sandstones etc. are examples.
2. **Basic refractories:** Lime, dolomite, magnesite etc. are examples.
3. **Neutral refractories:** Graphite, chromite, bone ash etc. are examples.

Silica (92% SiO_2 , 2.7% Al_2O_3) and quartz can tolerate temperature up to 1750°C , bauxite up to 2000°C , and magnesite, chromite, etc. up to 2200°C . Carbon carbides such as silicon carbide is used as refractory for special purposes.

1.16 SUMMARY OF OCCURRENCE AND EXTRACTION OF FEW ELEMENTS

Metal	Occurrence	Extraction Method	Remarks
Lithium	Spodumene [$(\text{LiAl}(\text{SiO}_3)_2)$]	Electrolysis of fused LiCl with KCl added to it. $\text{Li}^+ + e^- \rightarrow \text{Li}$	Because of their high reactivity they are extracted under anhydrous condition
Sodium	Rock salt (NaCl), feldspar ($\text{Na}_3\text{AlSi}_3\text{O}_8$), Chile saltpetre (NaNO_3)	Electrolysis of fused NaCl with CaCl_2 added to it. $\text{Na}^+ + e^- \rightarrow \text{Na}$	—do—
Potassium	Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)	Electrolysis of fused KCl with CaCl_2 added to it. $\text{K}^+ + e^- \rightarrow \text{K}$	—do—
Beryllium	Beryl ($3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$)	Electrolysis of fused BeF_2 with NaF added to it. $\text{Be}^{2+} + 2e^- \rightarrow \text{Be}$	—do—
Magnesium	Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) Magnesite (MgCO_3)	Electrolysis of fused MgCl_2 with KCl added to it. $\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$ Carbon reduction of MgO	Reduction using carbon is not possible with alkaline earths as they easily form carbides.

Calcium	Limestone (CaCO_3), (CaSO_4), dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$)	Electrolysis of fused CaCl_2 and CaF_2 mixture. $\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	—do—
Zinc	Zinc blende (ZnS), calamine (ZnCO_3), sphalerite (ZnS)	Reduction of ZnO with C or electrolysis of ZnSO_4 $\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}$	Zn metal can be purified by fractional distillation method.
Nickel	Millerite (NiS)	Reduction of NiO with CO $\text{NiO} + 5\text{CO} \rightarrow \text{Ni}(\text{CO})_4 + \text{CO}_2$ $\text{Ni}(\text{CO})_4 \rightarrow \text{Ni} + 4\text{CO}$	
Mercury	Cinnabar (HgS)	Direct reduction of HgS with heat alone. $\text{HgS} + \text{O}_2 \rightarrow \text{Hg} + \text{SO}_2$	
Chromium	Chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$)	Reduction of Cr_2O_3 with aluminium. $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3$	
Iron	Magnetite (Fe_3O_4), haematite (Fe_2O_3)	Reduction of oxides with CO . $\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$	
Bismuth	Bismuth glance (Bi_2O_3), bismuthite (Bi_2O_3)	Reduction of Bi_2O_3 with C . $\text{Bi}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Bi} + 3\text{CO}$	
Cobalt	Smattite (CoAs_2)	Reduction of Co_3O_4 with Al . $3\text{Co}_3\text{O}_4 + 3\text{Al} \rightarrow 9\text{CO} + 4\text{Al}_2\text{O}_3$	
Strontium	Strontianite (SrCO_3), celestine (SrSO_4)	Electrolysis of fused SrCl_2 $\text{Sr}^{2+} + 2e^- \rightarrow \text{Sr}$	
Barium	Witherite (BaCO_3), barytes (BaSO_4)	Electrolysis of fused BaCl_2 . $\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$	
Aluminium	Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), cryolite (Na_3AlF_6), aluminosilicates	Electrolysis of Al_2O_3 in molten Na_3AlF_6 (cryolite) or in Na_3AlCl_6 . $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	A good source of electricity is needed in the extraction of Al .
Manganese	Pyrolusite (MnO_2), Hausmannite (Mn_3O_4)	Reduction of oxide with Al or C . $3\text{Mn}_3\text{O}_4 + 8\text{Al} \rightarrow 4\text{Mn} + 4\text{Al}_2\text{O}_3$	

Titanium	Ilmenite (TiO ₂ ·FeO), rutile (TiO ₂)	Reduction of TiCl ₄ with Mg or Na. TiCl ₄ + 2Mg → Ti + 2MgCl ₂
Tin	Cassiterite (SnO ₂)	Reduction of SnO ₂ with C. SnO ₂ + 2C → Sn + 2CO
Lead	Galena (PbS)	Reduction of PbO with C. PbO + C → Pb + CO
Copper	Copper pyrites (CuFeS ₂), cuprite (Cu ₂ O)	Partial oxidation of sulphide ore. 2Cu ₂ O + Cu ₂ S → 6Cu + SO ₂
Silver	Argentite (Ag ₂ S), horn silver (AgCl), occur as metal	Leaching of sulphide ore using NaCN, followed by replacement of Ag by Zn. Ag ₂ S + 4NaCN → 2NaAg(CN) ₂ + Na ₂ S 2NaAg(CN) ₂ + Zn → 2Ag + Na ₂ Zn(CN) ₄
Gold	Occurs as metal	Same method as used in the case of silver.

ILLUSTRATION 1.8

- What is a slag?
- Give the principle of zone refining?
- An ore sample of galena (PbS) is contaminated with zinc blende (ZnS). Give an example of a chemical which can be used to concentrate galena selectively by froth flotation process.
- What is meant by the term 'Pyrometallurgy'?

Sol.

- Slag is a easily fusible material formed when gangue still present in the roasted or calcinated ore combines with the flux.
- When the melt of an impure metal is allowed to cool, the pure metal crystallises out while the impurities remain in the solution.
- Sodium cyanide, NaCN, can be used to concentrate galena selectively by froth flotation process.
- The process of extracting the metal by heating the metal oxide with a suitable reducing agent is known as pyrometallurgy.

ILLUSTRATION 1.9

- Indicate the temperature at which carbon can be used as reducing agent for FeO.
- Define flux.
- Metal usually do not occur in nature as nitrates. Why?
- Metal such as Cu, Ag, Zn etc. occur in nature as sulphides rather than oxides. Why?

Sol.

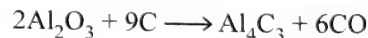
- At 1073 K or above, the standard free energy of formation of CO from C is much below the standard free energy of formation of FeO. Hence, above 1073 K, carbon can reduce FeO to Fe.
- Flux is a substance that combines with gangue, which may still be present in the roasted or calcinaed ore to form an easily fusible material called slag.
- Nitrates of all metals are soluble in water. Hence, if metal nitrates are present in the crust of earth, these would be slowly and gradually washed by rain water into the sea. Hence, metals usually do not occur in nature as nitrates.
- The cations of Cu, Ag and Zn, i.e. Cu⁺, Ag⁺ and Zn²⁺ [pseudo inert gas configuration, (ns²p⁶d¹⁰)] have high polarising power and hence easily polarises the bigger sulphide (S²⁻) ion than the small oxide (O²⁻) ion. Hence, sulphides of these metals are more stable than the oxides and these metals occur in nature as sulphides rather than oxides.

ILLUSTRATION 1.10

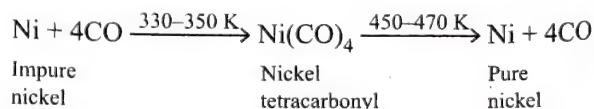
- Which of the following metals cannot be extracted by the smelting process?
Al, Zn, Fe and Pb.
- Graphite is used as an anode but not diamond. Give reason.
- Give a method for separation of nickel from cobalt?

Sol.

- Aluminium cannot be extracted by the smelting process because:
 - Al is a highly electropositive element and has strong affinity for oxygen. Hence, Al₂O₃ is a very stable compound and is not reduced by carbon.
 - Al₂O₃ on heating with carbon forms aluminium carbide (Al₄C₃).



- Graphite is a good conductor of electricity due to presence of free electrons within its layers, which help in conduction of electricity. Hence, graphite can be used as an anode. Whereas, diamond is a bad conductor of electricity due to absence of free electrons in its structure. Hence, diamond cannot be used as an anode.
- Nickel (Ni) can be separated from cobalt (Co) by Mond's process. CO is passed over a heated mixture of Ni and Co at 330–350 K, when Ni forms volatile Ni(CO)₄ but Co does not. The volatile Ni(CO)₄ is separated and then heated at 450–470 K to get pure Ni.



CONCEPT APPLICATION EXERCISE 1.3

1. Name the chief ores of tin, iron and aluminium. What methods are employed for the concentration/purification of their ores?
2. How do non-metals occur in nature? How are they extracted/isolated from their natural sources?
3. Giving appropriate examples (at least three), explain how the reactivity of a metal is related to its mode of occurrence in nature.
4. Describe the principle of froth flotation process. What is the role of a stabiliser and of a depressant? Give one example of each.
5. Name three ores which are concentrated by froth flotation process. What is a depressant?
6. Copper and silver lie below hydrogen in electrochemical series and yet they are found in the combined state as sulphides in nature. Comment.
7. Discuss some of the factors which need consideration before deciding on the method of extraction of metal from its ore.
8. Name three metals which are obtained by the reduction of their oxides though they do not occur as such in the earth's crust.
9. What do you understand by the following terms?
 - a. Roasting
 - b. Calcination
 - c. Smelting
10. Name the metals which are associated with the following terms in their extraction from their ores:
 - a. Bessemer's converter
 - b. Blast furnace
 - c. Aluminothermic process
 - d. Magnetic separation
11. Name the main steel plants which are operated by the Steel Authority of India.
12. Which metals are generally extracted by the electrolytic processes? What positions these metals generally occupy in the periodic table?
13. What are necessary conditions for refining a metal by Van Arkel and Mond's process?
14. In column chromatography which compounds acts as (i) stationary phase (ii) mobile phase and (iii) which compound is eluted first?
15. How Cl_2 is extracted from brine and why external e.m.f. is required in this process.

Solved Examples

EXAMPLE 1.1

Why is it advantageous to roast a sulphide ore to the oxide before reduction?

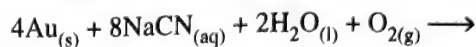
Sol. The standard free energies of formation, $\Delta_f G^\ominus$ of most of the sulphides are more negative than those of CS_2 and H_2S (CS_2 , in fact, is an endothermic compound). Therefore, neither carbon nor hydrogen can reduce metal sulphides to metal. In contrast, the standard free energies of formation of oxides are much lower

than that of SO_2 and hence oxidation of metal sulphides to metal oxides is thermodynamically favourable. Moreover, the free energies of formation of these metal oxides are less negative than that of CO and hence carbon can easily reduce these oxides to the corresponding metals.

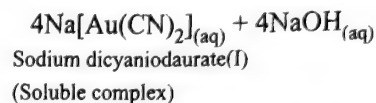
EXAMPLE 1.2

The extraction of Au by leaching with NaCN involves both oxidation and reduction. Justify giving equations.

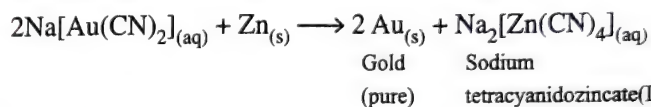
Sol. During leaching process, Au is first oxidised to Au^\oplus by O_2 of the air, which then combines with CN^\ominus ions to form the soluble complex, sodium dicyanidaurate(I).



Gold (impure)



Gold is then extracted from this complex by displacement method using a more electropositive zinc metal. In this reaction, Zn acts as a reducing agent. It reduces Au^\oplus to Au while it itself gets oxidised to Zn^{2+} , which combines with CN^\ominus ions to form a soluble complex, sodium tetracyanidozincate(II).



Thus, extraction of Au by leaching with NaCN involves both oxidation and reduction.

EXAMPLE 1.3

Free energies of formation ($\Delta_f G^\ominus$) of $\text{MgO}(\text{s})$ and $\text{CO}_{(\text{g})}$ at 1273 K and 2273 K are given below:

$$\Delta_f G^\ominus (\text{MgO}_{(\text{s})}) = -941 \text{ kJ/mol at } 1273 \text{ K}$$

$$\Delta_f G^\ominus (\text{MgO}_{(\text{s})}) = -314 \text{ kJ/mol at } 2273 \text{ K}$$

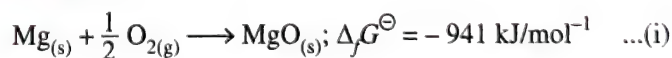
$$\Delta_f G^\ominus (\text{CO}_{(\text{g})}) = -439 \text{ kJ/mol at } 1273 \text{ K}$$

$$\Delta_f G^\ominus (\text{CO}_{(\text{g})}) = -628 \text{ kJ/mol at } 2273 \text{ K}$$

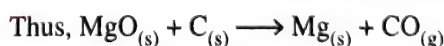
On the basis of above data, predict the temperature at which carbon can be used as a reducing for agent $\text{MgO}_{(\text{s})}$.

Sol.

a. At 1273 K

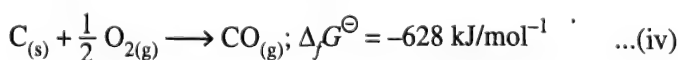
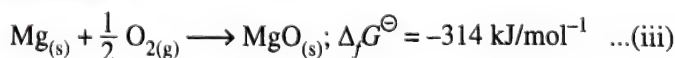


The redox equation for reduction of MgO to Mg by C can be obtained by subtracting Eq. (i) from Eq. (ii).

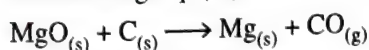


Since $\Delta_f G^\ominus$ of the above reduction reaction is +ve, reduction of MgO by C is not feasible at 1273 K.

b. At 2273 K



Subtracting Eq. (iii) from Eq. (iv), the redox equation is

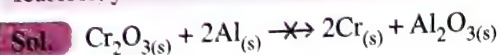


$$\begin{aligned}\Delta_f G^\ominus &= \Delta_f G^\ominus (\text{products}) - \Delta_f G^\ominus (\text{reactants}) \\ &= \Delta_f G^\ominus \text{CO}_{(g)} - \Delta_f G^\ominus \text{MgO}_{(s)} \\ &= (-628) - (-314) = -314 \text{ kJ mol}^{-1}\end{aligned}$$

Since $\Delta_f G^\ominus$ for the above reduction reaction is -ve, reduction of MgO by carbon at 2273 K is feasible.

EXAMPLE 1.4

Give reason: Reduction of Cr_2O_3 with Al is thermodynamically feasible, yet it does not occur at room temperature.

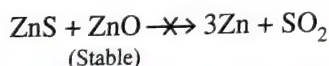
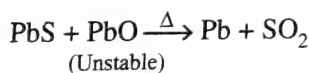
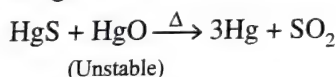


The interpretation of $\Delta_f G^\ominus$ is dependent on K ($\Delta G = -RT \ln K$) the equilibrium constant. Since in the abovementioned reaction all the reactants and products are solids at room temperature, there does not exist any equilibrium between the reactants and the products. That is why the reaction does not occur at room temperature. However, at higher temperature, when chromium (Cr) melts, value of $T\Delta S$ increases ($\Delta_f G^\ominus = \Delta_f H^\ominus - T\Delta_f S^\ominus$). As a result, $\Delta_f G^\ominus$ becomes more negative and hence the reaction proceeds rapidly.

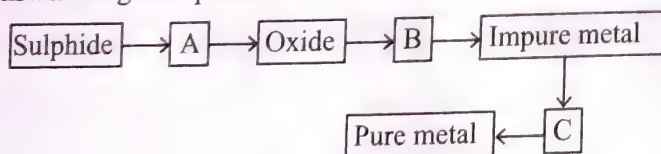
EXAMPLE 1.5

Cinnabar (HgS) and galena (PbS) on roasting often give their respective metals, but zinc blende (ZnS) does not. Give reason.

Sol. On roasting, all these sulphide ores are partly converted into their respective oxides. Since the oxides of mercury and lead are unstable while that of zinc is stable, oxides of mercury and lead bring about the reduction of their respective sulphides to the corresponding metals, but zinc oxide does not reduce ZnS to Zn.

**EXAMPLE 1.6**

From the following flowsheet for the extraction of pure metal, answer the given questions.



i. Step A is:

- Roasting
- Smelting
- Calcination
- Bessemerisation

ii. Step B (reduction) can be carried out by using:

- Carbon
- More electropositive element
- Both of these
- None of these

iii. Impure Cu metal is also obtained:

- By self-reduction during roasting of CuS
- By reduction of CuO with H_2

- By reduction of CuO with Al
 - By electrolysis of Cu^{2+} solution
- iv. Some of the following metals are obtained by electrolysis of their fused salts: Al, Na, Cu, Ag, Mg, Ca. These metals are:

- Cu, Ag
- Al, Na, Cu
- Ag, Mg, Ca
- Al, Na, Mg, Ca

v. Reduction of oxides to elements with carbon generally takes place at high temperature, hence Al is used in aluminothermite process. It is because:

- Al is more electropositive than the other metals (to be formed by reduction).
- Al has maximum affinity for oxygen.
- Reduction is highly exothermic, and the heat liberated makes the process spontaneous.
- Reduction is highly endothermic, and the heat absorbed makes the process spontaneous.

vi. Following reaction is not involved in thermite process:

- $3\text{Mn}_2\text{O}_4 + 8\text{Al} \longrightarrow 9\text{Mn} + 4\text{Al}_2\text{O}_3$
- $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$
- $2\text{Fe} + \text{Al}_2\text{O}_3 \longrightarrow 2\text{Al} + \text{Fe}_2\text{O}_3$
- $\text{B}_2\text{O}_3 + 2\text{Al} \longrightarrow 2\text{B} + \text{Al}_2\text{O}_3$

vii. Match column (A) (process) with column (B) (electrolyte)

A (Process)		B (Electrolyte)	
I	Down's cells process	W	Fused MgCl_2
II	Dow sea water process	X	Fused $(\text{Al}_2\text{O}_3 + \text{Na}_3\text{AlF}_6)$
III	Hall-Heroult process	Y	Fused KHF_2
IV	Moissan process	Z	Fused (40% NaCl + 60% CaCl_2)

Choose the correct answer:

- I II III IV I II III IV
- a. Z W X Y b. X Y Z W
- c. W Z X Y d. X Z W Y

viii. Match the method in column (X) with related reaction in column (Y).

Method (X)		Method (Y)	
I	Mond's process	A	$\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$
II	van Arkel-deBoer process	B	$\text{TiCl}_4 + 2\text{Mg} \xrightarrow{1000-1150^\circ\text{C}} \text{Ti} + 2\text{MgCl}_2$
III	Thermite process	C	$\text{Ni}(\text{CO})_4 \xrightarrow{230^\circ\text{C}} \text{Ni} + 4\text{CO}$
IV	Kroll process	D	$2\text{CuO} + \text{CuS} \longrightarrow 3\text{Cu} + \text{SO}_2$
V	Self reduction	E	$\text{ZrI}_4 \xrightarrow{\Delta} \text{Zr} + 2\text{I}_2$

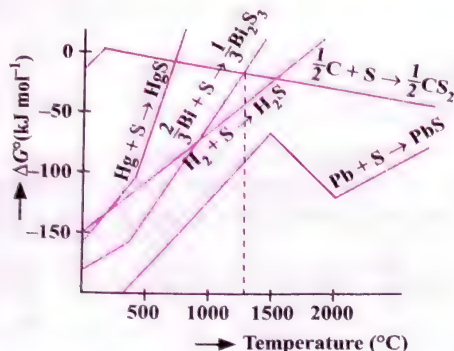
Choose the correct option:

	I	II	III	IV	V
a	A	B	C	D	E
b	D	C	B	A	E
c	C	E	A	B	D
d	B	D	E	C	B

- Sol.** i. a ii. c iii. a, b iv. d
v. a, c vi. c vii. a viii. c

EXAMPLE 1.7

The Ellingham diagram for a number of metallic sulphides is reproduced below.



Answer the questions given below:

- Formation of which of the sulphides is not spontaneous?
 - HgS
 - Bi₂S₃
 - PbS
 - CS₂
- Which occurs to minimum extent in nature?
 - HgS
 - H₂S
 - Bi₂S₃
 - CS₂
- Which of the following sulphides can be reduced to metal by H₂ at about 1000°C?
 - HgS
 - PbS
 - Bi₂S₃
 - All of these

Sol.

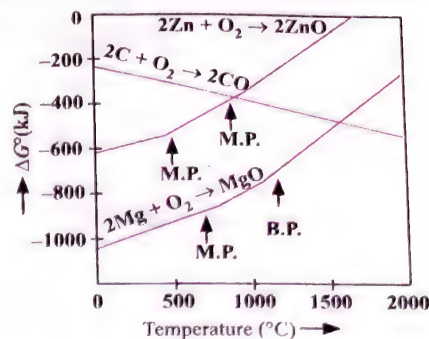
- (i) (c) $\Delta_f G^\ominus$ for PbS is lowest (i.e., more negative) therefore its formation is most spontaneous.
- (ii) (d) $\Delta_f G^\ominus$ for CS₂ is more -ve value at high temperature. This implies that formation of CS₂ is very stable and does not decomposes at high temperature.
- Since its formation from C & S, is very stable, so CS₂ exist in nature to minimum extent.
- (iii) (b) At 1000°C, $\Delta_f G^\ominus$ (H₂S) > $\Delta_f G^\ominus$ (PbS) therefore PbS can be reduced to Pb by H₂
- $$\text{PbS} + \text{H}_2 \rightarrow \text{Pb} + \text{H}_2\text{S}$$

EXAMPLE 1.8

Questions given below are based on the given diagram for extractive metallurgy.

- At what approximate temperature, zinc and carbon have equal affinity for oxygen?
 - 1000°C
 - 1500°C
 - 500°C
 - 1200°C
- At this temperature $\Delta_r G^\ominus$ of the reaction is

$$\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$$
 - ve
 - +ve
 - Zero
 - Nothing can be said



- To make the following reduction process spontaneous, temperature should be:

$$\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$$
 - < 1000°C
 - > 1000°C
 - < 500°C
 - > 500°C but < 1000°C
- At 1100°C, which reaction is spontaneous to a maximum extent?
 - $\text{MgO} + \text{C} \longrightarrow \text{Mg} + \text{CO}$
 - $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$
 - $\text{MgO} + \text{Zn} \longrightarrow \text{Mg} + \text{ZnO}$
 - $\text{ZnO} + \text{Mg} \longrightarrow \text{MgO} + \text{Zn}$
- This method is known as:
 - Pyrometallurgy
 - Parametallurgy
 - Hydrometallurgy
 - Semimetallurgy

Sol.

- (a) At ~1000°C, lines (C, CO) and (Zn, ZnO) intersect; at this temperature zinc and carbon have equal affinity for oxygen.
- (c) At ~1000°C, since Zn and C have equal affinity for O₂, $\Delta_r G^\ominus$ of the reaction is zero.

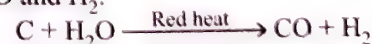
$$\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$$
- (b) To make the reaction

$$\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$$
 to proceed in forward direction, temperature should be greater than 1000°C.
- (d) At 1100°C, $\Delta_r G^\ominus$ for the reaction

$$\text{ZnO} + \text{Mg} \longrightarrow \text{MgO} + \text{Zn}$$
 has highest negative value, hence this reaction will be spontaneous to a maximum.
- (a)

EXAMPLE 1.9

At high temperature, carbon reacts with water to produce a mixture of CO and H₂.



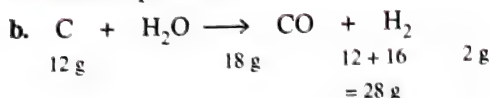
CO is separated from H₂ and then used to separate Ni from CO by forming a volatile compound, nickel tetracarbonyl (Ni(CO)₄).



- Formation of volatile Ni(CO)₄ and its subsequent heating give pure Ni. Name the process involved.
- How many moles of Ni(CO)₄ could be obtained from CO produced by the reaction of 75.0 g of carbon?

Sol.

a. Mond's process.



12 g of C reacts to produce 28 g of CO

75 g of C will react to produce

$$\frac{28}{12} \times 75 \text{ g of CO} = 175 \text{ g of CO} = \frac{175}{28} \text{ mol of CO} \\ = 6.25 \text{ moles of CO}$$

Since 4 mol of CO produces 1 mol of $\text{Ni}(\text{CO})_4$,

6.25 mol of CO will produce

$$\frac{1}{4} \times 6.25 \text{ mol of Ni}(\text{CO})_4 = 1.5625 \text{ mol of Ni}(\text{CO})_4.$$

Hence, 1.5625 mol of $\text{Ni}(\text{CO})_4$ could be obtained from CO produced by the reaction of 75.0 g of carbon.**EXAMPLE 1.10**

Colourless gas

When the colourless gas (B) is passed through lime water, initially a milky solution is obtained and on excess passage of gas (B) through the lime water, milky solution disappears.

i. (A) is:

- | | |
|----------------------------------------|----------------------------------------|
| a. CaCO_3 | b. MgCO_3 |
| c. $\text{CaCO}_3 \cdot \text{MgCO}_3$ | d. $\text{CaSO}_4 \cdot \text{MgCO}_3$ |

ii. (B) is

- | | |
|------------------|------------------|
| a. CO_2 | b. SO_2 |
| c. CO | d. SO_3 |

iii. Name of the product (A) is:

- | | |
|--------------|--------------|
| a. Dolomite | b. Limestone |
| c. Magnesite | d. Malachite |

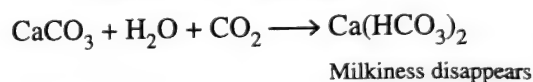
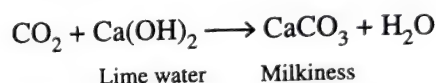
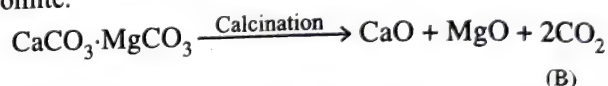
iv. Lime water is

- | | |
|--------------------|-------------------------------------------------|
| a. CaO | b. $\text{Ca}(\text{OH})_2$ |
| c. CaCO_3 | d. $\text{CaCO}_3 \cdot \text{Ca}(\text{OH})_2$ |

v. Milky solution of lime water disappears due to the formation of:

- | | |
|-----------------------------|--------------------------------|
| a. CaCO_3 | b. $\text{Ca}(\text{HCO}_3)_2$ |
| c. $\text{Ca}(\text{OH})_2$ | d. CaCl_2 |

Sol. Since on calcination, i.e., heating the ore (A) in limited supply of O_2 , both CaO and MgO are formed along with a colourless gas (B). (A) is $\text{CaCO}_3 \cdot \text{MgCO}_3$. (A) is known as dolomite.



On passing CO_2 through lime water [$\text{Ca}(\text{OH})_2$] solution, initially lime water turns milky due to formation of CaCO_3 , which is insoluble in water. On excess passage of CO_2 gas through lime water, milky solution disappears due to formation of $\text{Ca}(\text{HCO}_3)_2$. Hence,

i. c; A is $\text{CaCO}_3 \cdot \text{MgCO}_3$ ii. a; B is CO_2 iii. a; $\text{CaCO}_3 \cdot \text{MgCO}_3$ is known as dolomite.iv. b; Limewater is $\text{Ca}(\text{OH})_2$ solution.v. b; Milky solution disappears due to formation of $\text{Ca}(\text{HCO}_3)_2$.

Exercises

Single Correct Answer Type

Extraction of Metals Metallurgy

- The most abundant metal in the earth crust is
 - Al
 - Fe
 - Ca
 - Na
- The term "nuggets" refer to
 - An ore of Zn
 - An ore of boron
 - An ore which contains metal in the free state and lumps of almost pure metals are found in them.
 - The elements present in the 'core' are collectively known as "nuggets".
- Which metal is generally found in native state?
 - Cu
 - Au
 - Al
 - Fe
- A mineral is called ore if:
 - a metal can be extracted from it.
 - a metal can not be extracted from it.
 - a metal can be extracted profitably from it.
 - the metal present in the mineral is costly.
- Which of the following is true?
 - All ores are minerals
 - All minerals are ores
 - A mineral cannot be an ore
 - An ore cannot be a mineral
- The impurities present in the mineral are called
 - flux
 - gangue
 - alloy
 - slag
- Gold is extracted using:
 - Amalgamation process
 - Carbon reduction process
 - Electrolytic process
 - Oxidation process
- Carbon reduction is used for the extraction of:
 - Fe
 - K
 - Al
 - None of these
- Which is not a basic flux?
 - CaCO_3
 - CaO
 - SiO_2
 - None of these
- Metallurgy is the process of:
 - Concentrating the ore
 - Roasting of the ore
 - Adding carbon to the ore
 - Extracting the metal from the ore
- An essential constituent of amalgam is:
 - Hg
 - Ag
 - Au
 - Al
- Which element is not purified by zone refining?
 - Ge
 - Si
 - Ga
 - Ni
- Which element is found in human body?
 - Fe
 - Mg
 - Ca
 - Al
- Which group of oxides, the group containing oxides that cannot be reduced by carbon to give the respective metals is
 - Fe, Ca, Mg
 - Al, Mg, Ca
 - Fe, Ca
 - Ca, Mg
- Amongst the following groups of oxides, the group containing oxides that cannot be reduced by carbon to give the respective metals is
 - Cu_2O , SnO_2
 - Fe_2O_3 , ZnO
 - CaO , K_2O
 - PbO , Fe_3O_4
- Slag coming out at the bottom of a blast furnace during extraction of iron from its ore is used in making
 - Fertilisers
 - Roads
 - Plastics
 - Glass moulds
- Regions in which metals are found in earth is called
 - Lithophile
 - Atmophile
 - Calcophile
 - Siderophile
- Which furnace can be used to get temperature above 3000°C ?
 - Blast furnace
 - Reverberatory furnace
 - Arc furnace
 - None of the above
- Which is known as 'blister copper'?
 - Pure copper
 - 98% copper
 - Alloy of copper
 - Ore of copper
- Which process represents the following change, $\text{Ti} + 2\text{I}_2 \longrightarrow \text{TiI}_4 \longrightarrow \text{Ti} + 2\text{I}_2$?
 - Zone refining
 - Mond's process
 - Van Arkel method
 - Poling
- Following equation represents a method of purification of nickel by

$$\underset{\text{Impure}}{\text{Ni}} + 4\text{CO} \xrightarrow{320\text{ K}} \text{Ni}(\text{CO})_4 \xrightarrow[420\text{ K}]{\text{Pure}} \text{Ni} + 4\text{CO}$$
 - Mond's process
 - Van Arkel method
 - Zone refining
 - Cupellation
- The rocks formed by the solidification of magma over the years are
 - Igneous rocks
 - Sedimentary rocks
 - Metamorphic rocks
 - None of these
- The impurities associated with the ore after mining are collectively called
 - Flux
 - Slag
 - Minerals
 - Gangue
- An ore after levigation is found to have acidic impurities. Which of the following can be used as flux during smelting operation?
 - H_2SO_4
 - CaCO_3
 - SiO_2
 - Both CaCO_3 and SiO_2

24. The process in which metal oxide is reduced to metal by Al is called
 (1) Smelting (2) Aluminothermy
 (3) Hydrothermy (4) No specific name
25. Extraction of silver from Ag_2S by the use of sodium cyanide is an example of
 (1) Roasting (2) Hydrometallurgy
 (3) Electrometallurgy (4) Smelting.
26. Which of the following metals can be extracted by smelting?
 (1) Aluminium (2) Magnesium
 (3) Iron (4) None of these
27. The most abundant element in earth's crust is
 (1) Nitrogen (2) Oxygen
 (3) Iron (4) Magnesium
28. Which of the following processes involve the roasting process?
 (1) $\text{ZnCO}_3 \longrightarrow \text{ZnO} + \text{CO}_2$
 (2) $\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 2\text{Fe} + 3\text{CO}$
 (3) $2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2$
 (4) $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O}$
29. Alkali metals do not exist in free state in nature because these are
 (1) Very reactive
 (2) Very volatile
 (3) Metallic in nature
 (4) Highly electronegative elements
30. In the froth flotation process for beneficiation of ores, the ore particles float because
 (1) They are light
 (2) Their surface is not easily wetted by water
 (3) They bear electrostatic charge
 (4) They are insoluble
31. The salt which is least likely to be found in minerals is
 (1) Chloride (2) Sulphate
 (3) Sulphide (4) Nitrate
32. Which of the following beneficiation processes is used for the mineral $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$?
 (1) Froth flotation (2) Leaching
 (3) Liquation (4) Magnetic separation
33. In aluminothermite process, aluminium is used as
 (1) Oxidising agent (2) Flux
 (3) Reducing agent (4) Solder
34. Magnetic separation is used for increasing concentration of the:
 (1) Horn silver (2) Calcite
 (3) Haematite (4) Magnesite
35. Sulphide ores of metals are usually concentrated by froth flotation process. Which one of the following sulphide ores offers an exception and is concentrated by leaching?
 (1) Galena (2) Copper pyrite
 (3) Sphalerite (4) Argentite
36. Heating of ore in presence of air to remove impurity of sulphur is called
 (1) Calcination (2) Roasting
 (3) Smelting (4) None of these
37. Corundum is
 (1) SrO_2 (2) Al_2O_3
 (3) CaCl_2 (4) Cu_2Cl_2
38. Which ore can be best concentrated by froth flotation process?
 (1) Malachite (2) Cassiterite
 (3) Galena (4) Magnetite
39. The substance not likely to contain CaCO_3 is
 (1) Sea shells (2) Dolomite
 (3) Marble statue (4) Calcined gypsum
40. The incorrect statement is
 (1) Calamine and siderite are carbonates
 (2) Argentite and cuprite are oxides
 (3) Zinc blende and iron pyrites are sulphides
 (4) Malachite and azurite are ores of copper
41. Composition of malachite mineral is
 (1) $\text{CuCO}_3 \cdot \text{CuO}$ (2) $\text{Cu}(\text{HCO}_3)_2 \cdot \text{Cu}(\text{OH})_2$
 (3) $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (4) $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
42. Select the correct statement:
 (1) Calcination and roasting take place in reverberatory furnace, and small roasting takes place in small blast furnace
 (2) Calcination and roasting take place only in small blast furnace
 (3) Calcination and roasting take place only in reverberatory furnace
 (4) All are correct
43. During smelting, an additional substance is added which combines with impurities to form a fusible mass. The additional substance is called
 (1) Flux (2) Slag (3) Gangue (4) Ore
44. The process of isolation of metals by dissolving the ore in a suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called
 (1) Electrometallurgy (2) Hydrometallurgy
 (3) Electro refining (4) Zone refining
45. Complexes formed in the following methods are
 I. Mond's process for purification of nickel
 II. Removal of lead poisoning from the body
 III. Cyanide process for extraction of silver
 IV. Froth flotation process for separation of ZnS from galena ore by using depressant
- | I | II | III | IV |
|------------------------------|---------------------------------|------------------------------------|---------------------------------|
| (1) $\text{Ni}(\text{CO})_4$ | $[\text{Pb}(\text{EDTA})]^{2-}$ | $[\text{Ag}(\text{CN})_2]^\ominus$ | $[\text{Zn}(\text{CN})_2]$ |
| (2) $\text{Ni}(\text{CO})_4$ | $[\text{Pb}(\text{EDTA})]^{2-}$ | $[\text{Ag}(\text{CN})_4]^\ominus$ | $[\text{Zn}(\text{CN})_4]^{2-}$ |
| (3) $\text{Ni}(\text{CO})_6$ | $[\text{Pb}(\text{EDTA})]^{4-}$ | $[\text{Ag}(\text{CN})_2]^\ominus$ | $[\text{Zn}(\text{CN})_6]^{4-}$ |
| (4) $\text{Ni}(\text{CO})_4$ | $[\text{Pb}(\text{EDTA})]^{2-}$ | $[\text{Ag}(\text{CN})_4]^{3-}$ | $[\text{Zn}(\text{CN})_4]^{2-}$ |

46. Cassiterite ore consists of magnetic impurity named as
 (1) Chromite (2) Wolframite
 (3) Magnetite (4) Limonite
47. Which of the following process is not involved in the extraction of Fe?
 (1) Gravity separation (2) Leaching
 (3) Roasting (4) Carbon reduction
48. Chalcogens are
 (1) Hydrocarbons
 (2) Ore-forming elements
 (3) Oxide-forming elements
 (4) Those having ability to catenate
49. The oxidation states of Cu and Fe in chalcopyrite are, respectively,
 (1) +2, +2 (2) +1, +2
 (3) +1, +3 (4) +2, +1
50. Copper can be extracted by hydrometallurgy but not zinc because
 (1) Copper is comparatively less active metal as its reduction potential is high. It can be displaced from solutions of Cu^{2+} ion by more active metals
 (2) Zn displaced from solution of Zn^{2+} ion, a more reactive metal than it, but then readily reacts with water forming their corresponding ions and evolve hydrogen gas
 (3) Both (a) and (b) are correct
 (4) Copper can never be extracted by hydrometallurgy
51. Which of the following statement is correct?
 (1) Roasting is unnecessarily done for Fe extraction because there is no sulphide ore
 (2) In the smelting step of Cu extraction, reduction of the ore takes place
 (3) Ores may not be mineral
 (4) Sphalerite is the ore of zinc
52. Consider the following statements:
 Roasting is carried out to
 a. Convert sulphide to oxide and sulphate
 b. Remove water of hydration
 c. Melt the ore
 d. Remove arsenic and sulphur impurities
 Of these statements:
 (1) a, b and c are correct (2) a and d are correct
 (3) a, b and d are correct (4) b, c and d are correct.

Ellingham Diagram

53. Select the correct statement.
 (1) Sodium cyanide is used as a depressant to separate lead sulphide from zinc sulphide.
 (2) Iron can reduce alumina to aluminium metal.
 (3) Substances which convert infusible impurities present in ores into fusible substances during smelting are called slag.
 (4) Zirconium is best refined by zone refining method.
54. Select the incorrect statement.
 (1) Impurities are more soluble in the melt than in the solid state of the metal.
 (2) In Bessemerisation of sulphide ore of copper, there is self-reduction giving copper metal.
 (3) Mercury is transported in containers made of iron.
 (4) The ore CuFeS_2 is used to extract iron metal.
 (5) It is possible to extract a metal from its oxide if the free energy of formation of the oxide of the reducing agent is lower than that of the oxidising agent.
55. Select the incorrect statement.
 (1) Pig iron is manufactured by using blast furnace.
 (2) Platinum, indium etc. are known as noble metals because they are inert towards many common reagents.
 (3) Wrought iron is the purest form of iron.
 (4) Passivity of iron is due to the formation of thin film of sulphides on its surface.
56. Select the correct statement.
 (1) Phenomenon of removing layers of basic oxides from metals before electroplating is called pickling.
 (2) In the manufacture of iron from haematite, limestone is added to act as flux.
 (3) An ore of tin containing FeCrO_4 is concentrated by hydrometallurgy.
 (4) Both (1) and (2)
57. Select the incorrect statement.
 (1) In froth flotation process, the ore particles float because their surface is hydrophilic.
 (2) Coating of zinc on iron objects is commonly known as galvanisation.
 (3) In electrorefining, the impure metal is made anode.
 (4) All are incorrect.
58. Which of the following statements about the advantage of roasting of sulphide ore before reduction is not true?
 (1) $\Delta_f G^\ominus$ of the sulphide is greater than CS_2 and H_2S
 (2) $\Delta_f G^\ominus$ is negative for roasting of sulphide ore to oxide
 (3) Roasting of the sulphide to oxide is thermodynamically feasible
 (4) Carbon and hydrogen are suitable reducing agents for metal sulphides
59. When the sample of Cu with Zn impurity is to be purified by electrolysis, the appropriate electrodes are
- | Cathode | Anode |
|-------------------|---------------|
| (1) Pure Zn | Pure Cu |
| (2) Impure sample | Pure Cu |
| (3) Impure Zn | Impure sample |
| (4) Pure Cu | Impure sample |
60. During the process of electrorefining of copper, some metals present as impurity settle down as anode mud. These are
 (1) Sn and Ag (2) Pb and Zn
 (3) Ag and Au (4) Fe and Ni
61. Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly?

- (1) CO_2 is more volatile than CS_2
- (2) Metal sulphides are thermodynamically more stable than CS_2
- (3) CO_2 is thermodynamically more stable than CS_2
- (4) Metal sulphides are less stable than the corresponding oxides

62. Ellingham diagram represents

- (1) Change of ΔG with temperature
- (2) Change of ΔH with temperature
- (3) Change of ΔG with pressure
- (4) Change of $(\Delta G - T\Delta S)$ with temperature

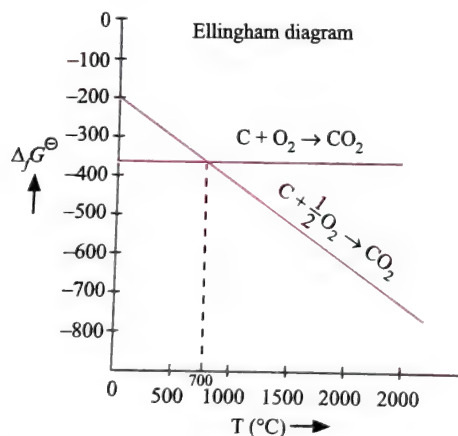
63. To carry out a reduction process, select a temperature so as to make

- (1) ΔG negative
- (2) ΔG positive
- (3) ΔH negative
- (4) ΔH positive

64. Select the correct statement.

- (1) The oxidation of CO into CO_2 will have a negative slope on Ellingham diagram.
- (2) Reduction of metal oxide is difficult if the metal formed is in liquid state at reduction temperature.
- (3) The reactive metals have negative slope for oxidation on Ellingham diagram whereas non-reactive metals have a positive slope
- (4) Reduction of metal oxide is normally less feasible at high temperature.

65.



Which of the following is incorrect on the basis of the above Ellingham diagram for carbon?

- (1) Up to 710°C , the reaction of formation of CO_2 is energetically more favourable, but above 710°C the formation of CO is preferred.
 - (2) In principle, carbon can be used to reduce any metal oxide at a sufficiently high temperature.
 - (3) $\Delta S[\text{C}_{(s)} + 1/2 \text{O}_{2(g)} \longrightarrow \text{CO}_{(g)}] < \Delta S[\text{C}_{(s)} + \text{O}_{2(g)} \longrightarrow \text{CO}_{2(g)}]$
 - (4) Carbon reduces many oxides at elevated temperature because ΔG° vs temperature line has a negative slope.
66. On heating a mixture of Cu_2O and Cu_2S , we get
- (1) $\text{Cu} + \text{SO}_2$
 - (2) $\text{Cu} + \text{SO}_3$
 - (3) $\text{CuO} + \text{CuS}$
 - (4) Cu_2SO_3

67. The method of zone refining of metals is based on the principle of

- (1) Greater solubility of the impurities in the molten state than in the solid
- (2) Greater solubility of pure metal than that of impurity
- (3) Higher melting point of the impurity than that of pure metal
- (4) Greater noble character of the solid metal than that of the impurity

68. Consider the following metallurgical processes:

- a. Heating impure metal with CO and distilling the resulting volatile carbonyl (BP 43°C) and finally decomposing at 150°C to 230°C to get the pure metal
- b. Heating the sulphide ore in air until a part is converted to oxide and then further heating in the absence of air to let the oxide react with unchanged sulphide
- c. Electrolysing the molten electrolyte containing CaCl_2 to obtain the metal

The processes used for obtaining sodium, nickel, and copper are, respectively

- (1) a, b and c
- (2) b, c and a
- (3) c, a and b
- (4) b, a and c

69. Complex formation for cyanide method is used for the extraction of

- (1) Cu
- (2) Fe
- (3) Hg
- (4) Ag

70. The least stable oxide at room temperature is

- (1) ZnO
- (2) CuO
- (3) Sb_2O_3
- (4) Ag_2O

71. High purity copper metal is obtained by

- (1) Carbon reduction
- (2) Hydrogen reduction
- (3) Electrolytic reduction
- (4) Thermite process

72. The metal extracted by leaching with cyanide is

- (1) Mg
- (2) Ag
- (3) Cu
- (4) Na

73. When MnO_2 is fused with KOH, a coloured compound is formed; the compound and its colour are

- (1) K_2MnO_4 , purple green
- (2) KMnO_4 , purple
- (3) Mn_2O_3 , brown
- (4) Mn_3O_4 , black

74. By which process Pb and Sn are extracted, respectively?

- (1) Carbon reduction, self-reduction
- (2) Self-reduction, carbon reduction
- (3) Electrolytic reduction, cyanide process
- (4) Cyanide process, electrolytic reduction

75. Extraction of Ag from commercial lead is possible by

- (1) Parke's process
- (2) Clarke's process
- (3) Pattinson's process
- (4) Electrolytic process

76. The chemical composition of slag formed during the smelting process in the extraction of copper is

- (1) $\text{Cu}_2\text{O} + \text{FeS}$
- (2) FeSiO_3
- (3) CuFeS_2
- (4) $\text{Cu}_2\text{S} + \text{FeO}$

77. The metal that cannot be obtained by electrolysis of the aqueous solution of their salts is
 (1) Ag (2) Mg
 (3) Cu (4) Cr
78. Ferric oxide in blast furnace is reduced by
 (1) C (2) CO
 (3) H₂ (4) CO₂
79. Electric furnaces are lined with magnesia because
 (1) It melts at a very high temperature
 (2) It is not affected by acids
 (3) It has no effect of electricity
 (4) It liberates oxygen on heating
80. Furnaces are lined with calcium oxide as
 (1) It gives light on heating (2) It is refractory and basic
 (3) It is not affected by acids (4) It gives O₂ on heating
81. The economical and high melting point compound used in furnace lining is
 (1) PbO (2) CaO
 (3) HgO (4) ZnO
82. In the reverberatory furnace
 (1) The flames are in contact with the charge
 (2) The flames do not come in contact with the charge
 (3) Only hot gases come in contact with the charge
 (4) The flames are not at all there
83. On heating limestone, carbon dioxide is given off. This operation in metallurgy is known as
 (1) Calcination (2) Roasting
 (3) Smelting (4) Ore-dressing
84. Pig iron is converted into steel by decreasing the amount of carbon present in it in a
 (1) Bessemer converter (2) Pyrite burner
 (3) Blast furnace (4) None of these
85. Rutile is an ore of
 (1) Ti (2) Mn
 (3) Ca (4) Mg
86. Iron obtained from blast furnace is known as
 (1) Steel (2) Cast iron
 (3) Wrought iron (4) Pig iron
87. Which does not contain aluminium?
 (1) Bauxite (2) Corundum
 (3) Diaspore (4) Dolomite
88. Which is not a silver ore?
 (1) Argentite (2) Siderite
 (3) Horn silver (4) Ruby silver
89. Sandstone in some iron ores is removed by
 (1) Carbon filters (2) Compressed air
 (3) Limestone (4) Sulphuric acid
90. Coating of zinc on iron objects is commonly known as
 (1) Galvanisation (2) Surface coating
 (3) Electroplating (4) Hydroplating
91. Blood of human beings contain
 (1) Fe (2) Mg
 (3) Co (4) Al
92. Which is not an ore of iron?
 (1) Magnetite (2) Haematite
 (3) Limonite (4) Cuprite
93. Lepidolite is an ore of
 (1) K (2) Na
 (3) Li (4) All of these
94. Granulated zinc is obtained by
 (1) Suddenly cooling molten zinc
 (2) Adding molten zinc to water
 (3) Heating zinc to 150°C
 (4) Dropping molten zinc drop by drop
95. Which is not an ore of lead?
 (1) Galena (2) Cassiterite
 (3) Anglesite (4) Cerussite
96. Tin is extracted from tin stone by heating it in a furnace with
 (1) CaCO₃ (2) Coal
 (3) CaO (4) Steam
97. Spelter is
 (1) Impure zinc (2) Impure iron
 (3) Pure zinc (4) Impure aluminium
98. CO on passing over heated nickel gives
 (1) Ni(CO)₄ (2) NiCO₃
 (3) CO + H₂ (4) CO₂ + H₂
99. The smelting of iron in a blast furnace involves all the steps except
 (1) Reduction (2) Fusion
 (3) Sublimation (4) Decomposition
100. Before introducing FeO in blast furnace, it is converted to Fe₂O₃ by roasting so that
 (1) It may not be removed as slag with silica
 (2) Oresence of it may increase the melting point of charge
 (3) It may not evaporate in the furnace
 (4) None of the above
101. During Bessemerisation of copper, the reaction taking place in the Bessemer convertor is
 (1) Cu₂S + 2Cu₂O → 6Cu + SO₂
 (2) Cu₂O + FeS → Cu₂S + FeO
 (3) FeO + SiO₂ → FeSiO₃
 (4) None of the above
102. Which metal is a liquid at room temperature?
 (1) Hg (2) K
 (3) Na (4) Ti
103. Which method is not correct for refining of crude metals?
 (1) Liquation: tin
 (2) Zone refining: silicon
 (3) Electrolytic refining: blister copper
 (4) Mond's process: aluminium

104. Which of the following combination represents the correct matching of metals with the most commonly employed ores for their extraction?

Fe	Zn	Cu	Al
(1) Haematite	Sphalerite	Copper pyrites	Bauxite
(2) Iron pyrites	Zincite	Cuprite	Clay
(3) Siderite	Calamine	Malachite	Aluminium phosphate
(4) Chalcocite	Magnetite	Copper glance	Bauxite

105. Which of the following benefaction process is used for the mineral $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$?

- (1) Froth flotation (2) Liquation
(3) Leaching (4) Magnetic separation

106. Heating mixture of Cu_2O and Cu_2S will give

- (1) $\text{Cu} + \text{SO}_2$ (2) $\text{Cu} + \text{SO}_3$
(3) $\text{CuO} + \text{CuS}$ (4) Cu_2SO_3

107. $\Delta_f G^\ominus$ vs T plot in the Ellingham diagram slopes downward for the reaction

- (1) $\text{Mg} + \frac{1}{2} \text{O}_2 \longrightarrow \text{MgO}$ (2) $2\text{Ag} + \frac{1}{2} \text{O}_2 \longrightarrow \text{Ag}_2\text{O}$
(3) $\text{C} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO}$ (4) $\text{CO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO}_2$

108. Which of the following reactions taking place in the blast furnace during extraction of iron is endothermic?

- (1) $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$
(2) $2\text{C} + \text{O}_2 \longrightarrow 2\text{CO}$
(3) $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$
(4) $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$

109. The ore having two different metal atoms is

- (1) Haematite (2) Galena
(3) Magnetite (4) Copper pyrites

110. Which of the following statements about the reduction is not true?

- (1) Roasting of the sulphide to the oxide is thermodynamically feasible
(2) Carbon and hydrogen are suitable reducing agents for metal sulphides
(3) The $\Delta_f G^\ominus$ is negative for roasting of sulphide ore to oxide
(4) The $\Delta_f G^\ominus$ of the sulphide is greater than those for CS_2 and H_2S

111. Among the metals Cr, Fe, Mn, Ti, Ba, and Mg, the one that cannot be obtained by reduction of metal oxide by aluminium is

- (1) Cr (2) Fe
(3) Mn (4) Mg

112. Extraction of zinc from zinc blende is achieved by

- (1) Electrolytic reduction
(2) Roasting followed by reduction with carbon

(3) Roasting followed by self-reduction

(4) Roasting followed by reduction with other metal

113. The incorrect statement among the following is

- (1) Hydrogen is used to reduce NiO
(2) Zirconium is refined by Van Arkel method
(3) The sulphide ore galena is concentrated by froth flotation
(4) In the metallurgy of iron, flux used is SiO_2

114. The auto-reduction process is not used in the metallurgy of

- (1) Hg (2) Cu
(3) Pb (4) Fe

115. Bauxite ore is made up of $\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{TiO}_2 + \text{Fe}_2\text{O}_3$. This ore is treated with conc. NaOH solution at 500 K and 35 bar pressure for a few hours and filtered hot. In the filtrate, the species present are

- (1) NaAl(OH)_4 only
(2) $\text{Na}_2\text{Ti(OH)}_6$ only
(3) NaAl(OH)_4 and Na_2SiO_3 both
(4) Na_2SiO_3 only

116. Identify the reaction that does not take place in a blast furnace.

- (1) $2\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 4\text{Fe} + 3\text{CO}_2$
(2) $\text{CO}_2 + \text{C} \longrightarrow 2\text{CO}$
(3) $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$
(4) $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$

117. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of

- (1) Nitrogen (2) Oxygen
(3) Carbon dioxide (4) Argon

118. When copper pyrites is roasted in excess of air, a mixture of $\text{CuO} + \text{FeO}$ is formed. FeO is present as impurity. This can be removed as slag during reduction of CuO . The flux added to form slag is

- (1) SiO_2 , which is an acidic flux
(2) Limestone, which is a basic flux
(3) SiO_2 , which is the basic flux
(4) CaO , which is a basic flux

119. Gold is extracted by hydrometallurgical process based on its property

- (1) Of being electropositive
(2) To form complexes, which are water soluble
(3) Of being less reactive
(4) To form salts, which are water soluble

120. Van Arkel method of purification of metals involves converting the metal to a

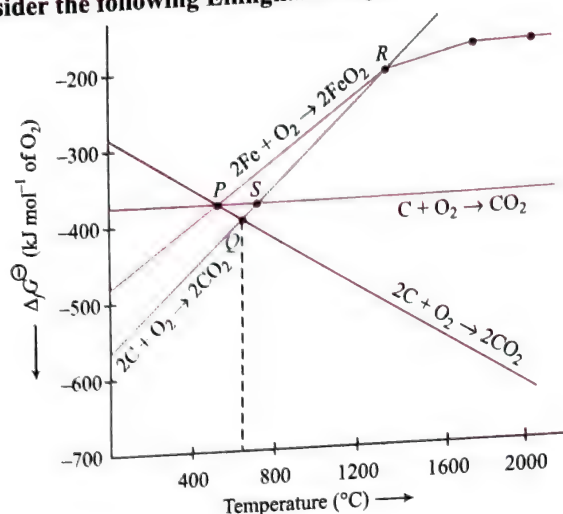
- (1) Volatile enough stable compound
(2) Volatile unstable compound
(3) Non-volatile stable compound
(4) None of these

121. Self-reduction of CuS to Cu can be carried out in

- (1) Bessemer converter (2) Blast furnace
(3) Both (1) and (2) (4) None of these

122. $\text{Ag}_2\text{S} + \text{NaCN} \longrightarrow (\text{A}), (\text{A}) + \text{Zn} \longrightarrow (\text{B})$
 B is a metal. Hence, (A) and (B) are
 (1) $\text{Na}_2[\text{Zn}(\text{CN})_4]$, Zn (2) $\text{Na}[\text{Ag}(\text{CN})_2]$, Ag
 (3) $\text{Na}_2[\text{Ag}(\text{CN})_4]$, Ag (4) $\text{Na}_3[\text{Ag}(\text{CN})_4]$, Ag
123. Find the formula of A
 $\text{ZnS} + \text{O}_2 \longrightarrow (\text{A}) + \text{SO}_2$
 (1) ZnCO_3 (2) ZnS
 (3) ZnSO_4 (4) $\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$
124. Four metals and their methods of refinement are given
 i. Ni, Cu, Zr, Ga
 ii. Electrolysis, Van Arkel process, zone refining, Mond's process
 Choose the right method for each:
 (1) Ni: Electrolysis; Cu: Van Arkel process; Zr: Zone refining; Ga: Mond's process
 (2) Ni: Mond's process; Cu: Electrolysis; Zr: Van Arkel process; Ga: Zone refining
 (3) Ni: Mond's process; Cu: Van Arkel process; Zr: Zone refining; Ga: Electrolysis
 (4) Ni: Electrolysis; Cu: Zone refining; Zr: Van Arkel process; Ga: Mond's process
125. Which of the following statement is correct regarding Cu extraction?
 (1) In the smelting step, carbon reduction takes places
 (2) During roasting, Cu_2S remains almost unaffected
 (3) In Bessemer converter, only self-reduction occurs, not slag formation.
 (4) Blister formed in the blister Cu is due to dissolved CO_2
126. Carbon reduction process is not commercially applicable for which of the following set to oxides to extract the respective metal?
 I. ZnO II. Fe_2O_3 III. Al_2O_3 IV. SnO_2
 V. MgO
 (1) ZnO, Fe_2O_3 , SnO_2 (2) ZnO, SnO, MgO
 (3) MgO, Al_2O_3 (4) MgO, SnO, Al_2O_3
127. Which of the following metal can be reduced by carbon reduction as well as self-reduction?
 (1) Fe (2) Al
 (3) Pb (4) None of these
128. The method not used in metallurgy to refine impure metal is:
 (1) Mond's process (2) Van Arkel process
 (3) Liquation (4) All are used
129. Thermite reduction is not used for commercial extraction of the respective metal from which of the following oxides?
 (1) Mn_3O_4 (2) TiO_2
 (3) Fe_2O_3 (4) Cr_2O_3
130. Select the incorrect statement
 (1) Iron is the fifth most abundant element in the earth's crust.
 (2) Zinc blende is the ore of zinc.
 (3) Froth flotation process is generally employed for sulphide ores.
 (4) The most abundant metal in earth's crust is aluminium.
131. Select the incorrect statement
 (1) Extraction of aluminium from alumina is done by electrometallurgy.
 (2) The metals like Si, Ga, etc., which are used in semi-conductors, are purified by zone refining.
 (3) The purification of crude metal is referred to refining.
 (4) Magnesite is an ore of Mn.
132. Select the incorrect statement
 (1) The metal present in chlorophyll is Ca
 (2) The process of reduction of oxides by aluminium is known as aluminothermy.
 (3) The process of removal of gangue from ore is known as concentration of ores.
 (4) Aluminium is obtained from Al_2O_3 by electrolytic reduction.
133. Select the incorrect statement
 (1) In the metallurgical process for electrorefining of the metal, the anode is made of impure metal.
 (2) Roasting is generally carried out in sulphide ores.
 (3) Gold is usually found in quartz mineral.
 (4) Metal extracted from sea water is Ca.
134. Select the incorrect statement
 (1) The naturally occurring chemical substances in form of which metals occur in the earth along with impurities are called minerals.
 (2) The earthy and siliceous impurities which generally occur with ores are called slag.
 (3) Highly reactive elements occur in nature in combined state.
 (4) Minerals from which metals are extracted conveniently and economically are called ores.
135. Select the incorrect statement
 (1) The complete process of extracting the metal from its ores is called metallurgy.
 (2) Calcination is the process of heating the ore strongly in the absence of air.
 (3) An ore of tin containing FeCrO_4 is concentrated by electromagnetic separation
 (4) Sodium cyanide solution is used to extract Ag or Al from its ores.
136. Select the incorrect statement
 (1) Sulphides ores are concentrated by froth flotation and roasted in excess of air to convert them into their respective oxides.
 (2) SiO_2 acts as an acidic flux while CaCO_3 acts as a basic flux.
 (3) In the metallurgy of copper, the flux used to remove the basic impurity of FeO is SiO_2
 (4) During extraction of iron from haematite, the flux used is SiO_2

Consider the following Ellingham diagram



137. Refer to the above Ellingham diagram.

At the temperature corresponding to which of the points in the above given diagram, FeO will be reduced to Fe by coupling the reaction $2\text{FeO} \rightarrow 2\text{Fe} + \text{O}_2$ with all of the following reactions?

- (i) $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ (ii) $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$
 (iii) $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$
 (1) Point P & R (2) Point Q and R
 (3) Point Q and S (4) Point P and S

138. Select the incorrect statement about Ellingham diagram.

- (1) According to Ellingham diagram, Aluminium will reduce MgO at temperature below 1350°C .
 (2) All oxides theoretically can not be decomposed to give the metal and O_2 , at sufficiently high temperature.
 (3) At high temperature, a point will be reached where the graph crosses the $\Delta_f G^\ominus$ line. Below this temperature, $\Delta_f G^\ominus$ of the oxides is negative, so the oxide is stable.
 (4) Any metal will not reduce the oxide of other metals which lie above it in the Ellingham diagram.

139. Select the incorrect statement about the reduction.

- (1) The $\Delta_f G^\ominus$ of the sulphide is greater than those for CS_2 and H_2S .
 (2) C and H_2 are suitable reducing agents for metal sulphides.
 (3) Roasting of the sulphides to the oxides is thermodynamically feasible.
 (4) The $\Delta_f G^\ominus$ is negative for roasting of sulphide ore to oxide.

140. Refer to Ellingham diagram in Q.138. Select the correct option. Below point P, FeO can

- (1) not be reduced by both C and CO.
 (2) be reduced by CO only
 (3) be reduced by both CO and C.
 (4) be reduced by C only.

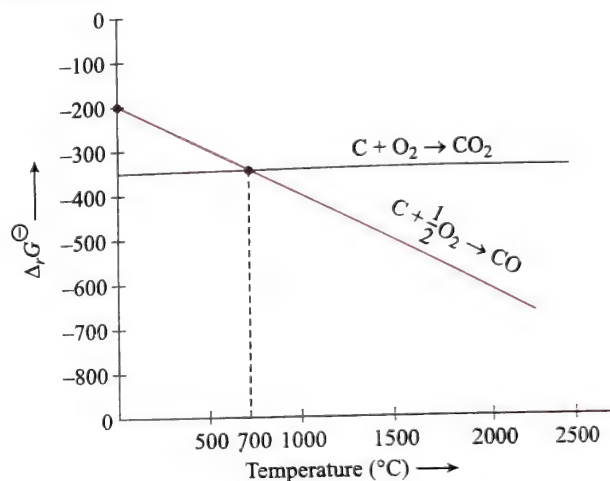
141. Refer to Ellingham diagram in Q.138. Select the correct option. For the reduction of FeO at the temperature at point R is:

- (1) ΔG^\ominus value for the overall reduction reaction with CO is negative.
 (2) ΔG^\ominus value for the overall reduction reaction with a mixture of a 1 mol of C and 1 mol O_2 is positive.
 (3) ΔG^\ominus value for the overall reduction reaction with a 2 mol C and 1 mol of O_2 will be positive.
 (4) ΔG^\ominus value for the overall reduction reaction with CO is zero.

142. Refer to Ellingham diagram in Q.138. The temperature at which C reduces FeO to give Fe and CO is

- (1) Above temperature at point P.
 (2) Above temperature at point P but below temperature at point R.
 (3) Below temperature at point P.
 (4) Approximately at temperature corresponding to point P.

143. On the basis of above Ellingham diagram, select the incorrect statement.



- (1) Carbon can be used to reduce any metal oxide at a high temperature.
 (2) Carbon reduces many oxides at elevated temperature because $\Delta_f G^\ominus$ is temperature line with negative slope.
 (3) $\Delta S(\text{C}, \text{CO}) < \Delta S(\text{C}, \text{CO}_2)$
 (4) Upto 710°C , formation of CO_2 is more favourable energetically but above 710°C , the formation of CO is preferred.

Multiple Correct Answers Type

1. Metallurgy involves steps:

- (1) Concentration of ore (2) Reduction of ore
 (3) Purification (4) Alloy formation

2. Which of the following ores is/are oxide ore(s)?

- (1) Cassiterite (2) Bauxite
 (3) Cryolite (4) Haematite

3. Which of the following are correctly matched?

- (1) Malachite : $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
 (2) Chalcopyrite : CuFeS_2
 (3) Copper glance : Cu_2S
 (4) Azurite : Cu_2O

4. Find the correct match:

	Column I	Column II
(1)	Azurite	$\text{CuCO}_3 \cdot 2\text{Cu(OH)}_2$
(2)	Malachite	$\text{Cu(OH)}_2 \cdot \text{CuCO}_3$
(3)	Anglesite	PbSO_4
(4)	Chalcocite	Cu_2S

5. Carnallite is an ore of

- (1) Sodium (2) Potassium
(3) Magnesium (4) Aluminium

6. Which is (are) not an ore?

- (1) Bauxite (2) Zinc blende
(3) Pig iron (4) Wrought iron

7. Salt which is (are) least likely to find in minerals

- (1) Acetate (2) Nitrate
(3) Chloride (4) Sulphate

8. Metal(s) which does/do not form amalgam is/are:

- (1) Fe (2) Zn
(3) Ni (4) Au

9. $\text{Ca}_3(\text{PO}_4)_2$ is:

- (1) Thomas slag
(2) Used in cement manufacturing
(3) Used in manufacture of phosphorus fertiliser
(4) Used as a refractory material

10. Which of the following pairs consists of ore of the same metal?

- (1) Magnesite, cerussite (2) Chalcocite, copper pyrites
(3) Bauxite, corundum (4) Anglesite, cerussite

11. Froth flotation process used for the concentration of sulphide ore

- (1) Is based on the difference in wettability of different minerals
(2) Uses sodium ethyl xanthate, $\text{C}_2\text{H}_5\text{OCS}_2\text{Na}$, as collector
(3) Uses NaCN as depressant in the mixture of ZnS and PbS when ZnS forms soluble complex and PbS forms froth
(4) Uses pine oil as frothing agent

12. Which of the following are correct processes?

- (1) $\text{Fe} + \text{Al}_2\text{O}_3 \longrightarrow 2\text{Al} + \text{Fe}_2\text{O}_3$
(2) $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$
(3) $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow 2\text{Cr} + \text{Al}_2\text{O}_3$
(4) $2[\text{Ag}(\text{CN})_2]^\ominus + \text{Zn} \longrightarrow 2\text{Ag} + [\text{Zn}(\text{CN})_4]^{2-}$

13. Which of the following reactions occur during calcination?

- (1) $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$
(2) $2\text{Al(OH)}_3 \longrightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$
(3) $4\text{FeS}_2 + 11\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$
(4) $\text{Cu}_2\text{S} + 2\text{CuO} \longrightarrow 4\text{Cu} + \text{SO}_2$

14. Leaching can be used for extraction of

- (1) Pb (2) Al
(3) Ag (4) Au

15. MgO can be used as a refractory material because

- (1) It is a good electrical insulator
(2) It is a good conductor of heat
(3) It has high melting point
(4) None of the above.

16. The extraction of metals from oxide ores involves

- (1) Reduction with carbon (2) Reduction with aluminium
(3) Electrolytic reduction (4) Reduction with CO

17. Which of the following oxides cannot be reduced to metal by carbon?

- (1) ZnO (2) Al_2O_3
(3) CuO (4) MgO

18. Which of the following statements are correct regarding metallurgy of iron?

- (1) Coke reduces FeO to Fe above 1073 K
(2) CO reduces Fe_2O_3 to FeO below 1073 K
(3) Coke reduces Fe_2O_3 to FeO above 1073 K
(4) Coke reduces Fe_2O_3 to FeO above 1073 K

19. The major role of fluorspar, CaF_2 which is added in small amount in the electrolytic reduction of Al_2O_3 dissolved in fused cryolite is

- (1) To increase the conductivity of the fused mixture
(2) To lower the fusion temperature of the melt
(3) To act as catalyst
(4) To decrease the rate of oxidation of carbon at the anode

20. Which is correct process–mineral group in metallurgical extraction?

- (1) Leaching: Ag (2) Van Arkel: Zr
(3) Liquefaction: Sn (4) Zone refining: Sn

21. Tempering of steel

- (1) Increases mechanical strength
(2) Changes ratio of iron in steel
(3) Involves heating the steel to appropriate temperature and then cooling it rapidly
(4) Decreases mechanical strength

22. Out of the following reduction processes:

- i. $\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 2\text{Fe} + 3\text{CO}$
ii. $\text{Cu}_2\text{O} + \text{C} \longrightarrow 2\text{Cu} + \text{CO}$
iii. $\text{PbO} + \text{C} \longrightarrow \text{Pb} + \text{CO}$
iv. $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$

Correct process is/are:

- (1) (i) (2) (ii)
(3) (iii) (4) (iv)

23. Which out of the following metals can be obtained by electrolysis of the aqueous solution of their salts?

- (1) Ag (2) Mg
(3) Au (4) Na

24. Auto-reduction process is used for the extraction of:

- (1) Cu (2) Hg
(3) Pb (4) Al

25. Disadvantages of using carbon as a reducing agent:

- (1) High temperature is needed
(2) Many metals combine with carbon to form carbides

- (3) Low temperature is needed
 (4) Many metals combine with carbon and do not form carbides
26. Select the correct statements:
 (1) Based on reactivity series, occurrence of certain elements takes place in native state
 (2) Due to the basic nature of oxides of alkaline earth metals, they combine with atmospheric acidic oxides giving salts
 (3) Based on reactivity series, occurrence of certain elements takes place in atomic state
 (4) None is correct
27. Which of the following steps are involved in hydrometallurgical process?
 (1) $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \longrightarrow 6\text{Cu} + \text{SO}_2$
 (2) $\text{CuFeS}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{S}$
 (3) $\text{Ag}_2\text{S} + 2\text{NaCN} \longrightarrow [\text{Ag}(\text{CN})_2]^\ominus + \text{Na}_2\text{S}$
 (4) $\text{CuCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O} + \text{CO}_2$
28. The reduction of an oxide by aluminium is not called
 (1) Ellingham process
 (2) Goldschmidt's aluminothermite process
 (3) Kroll's process
 (4) Van Arkel process
29. For the pyrometallurgical method used for the extraction of copper from sulphide ore, which statements is/are correct?
 (1) Pyrometallurgy is a dry method
 (2) It involves concentration by leaching the sulphide ore with dil. H_2SO_4
 (3) It involves concentration of the sulphide ore by froth flotation process
 (4) It involves concentration by leaching for every ore
30. In Fe extraction, the roasting is carried out because
 (1) All FeO be converted to Fe_2O_3
 (2) The formation of FeSiO_3 slag is prevented
 (3) Fe_2O_3 does not react with SiO_2 to form slag
 (4) The formation of slag (CaSiO_3) is enhanced
31. Which of the following metal oxides are reduced by self-reduction method?
 (1) Cu_2O (2) PbO
 (3) HgO (4) CaO
32. Select the correct statements:
 (1) In hydrometallurgy, Zn is used as oxidising agent in the purification of Ag from $[\text{Ag}(\text{CN})_2]^\ominus$.
 (2) When pine oil or eucalyptus oil is added into the water, it lowers down the surface tension by which froth is formed
 (3) Sodium ethyl xanthate is used as collector
 (4) Basic copper carbonate or PbSO_4 is concentrated by froth flotation method by using an activator
33. Select the correct statements for calcination:
 (1) Carbonate ore is converted in oxide ore
 (2) Hydrated oxide ore is converted into its oxide ore
 (3) Oxidisable volatile impurities are removed by calcination process
 (4) Only calcination occurs for carbonate or oxide ore
34. In the commercial extraction of iron, roasting is adopted because
 (1) It removes impurities of S, As, and Sb in the form of their elemental vapour
 (2) It prevents slag formation by Fe_2O_3
 (3) It prevents slag formation by FeO
 (4) Limonite is converted into its anhydrous form
35. Which of the following statements is/are correct?
 (1) The chemical processes in the production of steel from haematite ore involve reduction followed by oxidation
 (2) Lead is extracted from its chief ore galena by both carbon reduction as well as self-reduction
 (3) In Hall-Heroult process, the electrolyte used is a molten mixture of alumina and cryolite or fluorspar
 (4) Haematite, cassiterite and argentite are oxide ores
36. Liquation process may be applied for the purification of
 (1) Copper (2) Tin
 (3) Iron (4) Lead
37. The anode mud obtained during electrorefining of copper may contain
 (1) Iron (2) Magnesium
 (3) Silver (4) Gold
38. The extraction of metals from sulphide ore involves
 (1) Reduction with carbon (2) Froth flotation
 (3) Reduction with Al (4) Electrolytic reduction
39. H_2 is not widely used as the reducing agent in metallurgical process because
 (1) Many metals react with H_2 at elevated temperature forming hydrides
 (2) There is a risk of explosion from H_2 and O_2 present in the air
 (3) Reducing power of H_2 does not increase with temperature
 (4) Reducing power of H_2 increases with temperature
40. Select the correct statement.
 (1) Alkali metals are generally extracted by electrolysis of their ores in fused state.
 (2) Levigation is generally employed for concentration of sulphide ores.
 (3) Every mineral is an ore, but every ore is not a mineral.
 (4) Slag is a product formed during smelting by combination of flux and impurities.
41. Select the correct statement.
 (1) Alkali metals can be obtained by chemical reduction of their compounds.
 (2) Sylvine is an ore of potassium.
 (3) Oxide ores are purified by levigation process.
 (4) During electrorefining of a metal, impure metal is made anode.
42. Select the correct statement.
 (1) Highly pure metals can be obtained by zone refining.
 (2) Aluminium is the most abundant metal in the earth's crust.

- (3) Reactive metals occur in native state.
 (4) The process of calcination and roasting is carried out in reverberatory furnace.

43. Select the correct statement.

- (1) In calcination, ore is heated with calcium.
 (2) Copper is found both in free as well as in combined state in nature.
 (3) Below 1623 K, Al can reduce MgO to Mg, but above 1623 K, reverse is true.
 (4) Mond's process is used for purification of titanium.

44. Select the correct statements (Ellingham diagram):

- (1) When temperature is raised, a point will be reached where the graph crosses the $\Delta_f G^\ominus = 0$ line. Below this temperature, the free energy of formation of the oxide is negative, so the oxide is stable
 (2) When the temperature is raised, a point will be reached where the graph crosses the $\Delta_f G^\ominus = 0$ line. Above this temperature, the free energy of formation of the oxide is positive, and the oxide becomes unstable, and should decompose into the metal and dioxygen
 (3) Theoretically, all oxides can be decomposed to give the metal and dioxygen if a sufficiently high temperature can be attained
 (4) Theoretically, all oxides cannot be decomposed to give the metal and dioxygen if a sufficiently high temperature can be attained

45. Select the correct statements for Ellingham diagram:

- (1) Any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram
 (2) According to Ellingham diagram, Al will not reduce MgO at temperature below 1350°C
 (3) According to Ellingham diagram, Al will reduce MgO at temperature below 1350°C
 (4) Any metal will not reduce the oxide of other metals which lie above it in the Ellingham diagram

46. Select the correct statements for Ellingham diagram.

- (1) The slope of the curves of the formation of metal oxide is +ve because $\Delta_f G^\ominus$ becomes less negative or increases with the rise in temperature
 (2) Each curve is a straight line except when some change takes place in phase (s \rightarrow l or l \rightarrow g)
 (3) Each curve is not a straight line except when some change takes place in phase (s \rightarrow l or l \rightarrow g)
 (4) The slope of the curves of the formation of metal oxide is -ve because $\Delta_f G^\ominus$ becomes less negative or increases with the rise in temperature

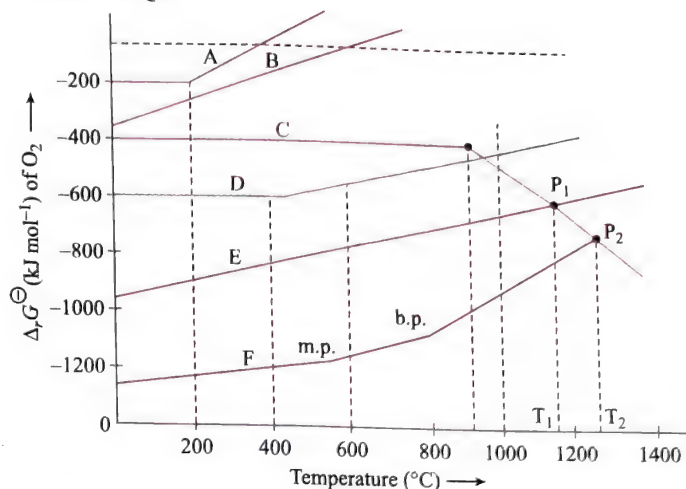
47. In the leaching of Ag_2S with NaCN, a stream of air is also passed. It is because of

- (1) Reversible nature of reaction between Ag_2S and NaCN
 (2) Oxidised Na_2S formed into Na_2SO_4
 (3) Irreversible nature of reaction between Ag_2S and NaCN
 (4) None of the above

48. Silver containing lead as an impurity is not purified by

- (1) Poling
 (2) Cupellation
 (3) Levigation
 (4) Distillation

For Q.49 to Q.51



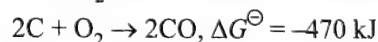
49. Refer to the above Ellingham diagram, select correct option.

- (1) Reduction of E_2O_3 to E is possible by C below 1000°C
 (2) At 500°C reduction of oxide of A, B is possible by C.
 (3) Extraction of D is possible reduction of its oxide by B and C
 (4) Below 400°C oxide of A should decompose into metal and O_2

50. Refer to above diagram. Which of the following reaction have $\Delta_f G^\ominus = 0$, at temperature T_2 and T_1 respectively.

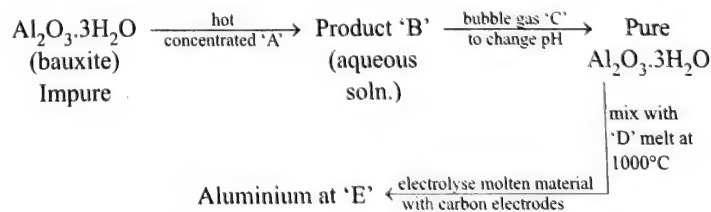
- (1) $\text{FO} + \text{C} \rightarrow \text{F} + \text{CO}$ (2) $\text{FO} + \text{D} \rightarrow \text{F} + \text{DO}$
 (3) $\text{EO} + \text{C} \rightarrow \text{E} + \text{CO}$ (4) $\text{EO} + \text{D} \rightarrow \text{E} + \text{DO}$

51. Refer to above diagram. Select the incorrect statement at 1000°C. Given



- (1) Reduction of DO is possible by C and metals are obtained in vapour state.
 (2) Reduction of DO is not possible by C
 (3) For reaction $\text{DO} + \text{C} \rightarrow \text{D} + \text{CO}$, $\Delta_f G^\ominus = +50 \text{ kJ}$
 (4) Metal C has more affinity for O_2 as compared to D.

52. In the extraction of aluminium metal, one of the process is summarised as follows:



Which of the following entries correctly summarises reagents, electrodes & products of the process?

- | A | B | C | D | E |
|-----------------------------|------------------------------|---------------|---------------------------|---------|
| (1) NaOH | Al^{3+} | HF | Na_3AlF_6 | Cathode |
| (2) NaOH | NaAlO_2 | CO_2 | NaF | Anode |
| (3) H_2SO_4 | $\text{Al}_2(\text{SO}_4)_3$ | NH | Na_3AlF_6 | Cathode |
| (4) NaOH | NaAlO_2 | CO_2 | Na_3AlF_6 | Cathode |

53. Of the following reduction processes, correct processes are:

- (1) $\text{Fe}_2\text{O}_3 + \text{C} \rightarrow \text{Fe}$ (2) $\text{ZnO} + \text{C} \rightarrow \text{Zn}$
 (3) $\text{Ca}_3(\text{PO}_4)_2 + \text{C} \rightarrow \text{P}$ (4) $\text{PbO} + \text{C} \rightarrow \text{Pb}$

54. Metals which can be extracted by smelting process are:

- (1) Pb (2) Fe
 (3) Zn (4) Al

55. Aluminothermy used for the spot welding of large iron structures is based upon the fact that:

- (1) As compared to iron, aluminium has greater affinity for oxygen
 (2) As compared to aluminium, iron has greater affinity for oxygen
 (3) Reaction between aluminium and oxygen is endothermic
 (4) Reaction between iron oxide and aluminium

56. Which of the following are true for electrolytic extraction of aluminium?

- (1) Cathode material contains graphite
 (2) Anode material contains graphite
 (3) Cathode reacts away forming CO_2
 (4) Anode reacts away forming CO_2

57. The chief reaction(s) occurring in blast furnace during extraction of iron from haematite is/are:

- (1) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$
 (2) $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$
 (3) $\text{Fe}_2\text{O}_3 + \text{C} \rightarrow 2\text{Fe} + 3\text{CO}$
 (4) $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$

58. Select correct statement regarding silver extraction process.

- (1) When the lead-silver alloy is rich in silver, lead is removed by the cupellation process
 (2) When the lead-silver alloy is rich in lead, lead is removed by parke's or pattinson's process
 (3) Zinc forms an alloy with lead, from which lead is separated by distillation
 (4) Zinc forms an alloy with silver, from which zinc is separated by distillation

59. Which of the following reduction reactions are actually employed in commercial extraction of metals?

- (1) $\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$
 (2) $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$
 (3) $2\text{Na}[\text{Au}(\text{CN})_2] + \text{Zn} \rightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Au}$
 (4) $\text{Cu}_2\text{S} + \text{Pb} \rightarrow \text{Cu} + \text{PbS} \downarrow$

60. Highly electropositive metals can not be extracted by carbon reduction process because these:

- (1) Metals combine with carbon to form carbides
 (2) Metals do not react with carbon
 (3) Metal oxides are not reduced by carbon
 (4) Loss of metal is more by vaporisation

(Cu_2O), copper glance (Cu_2S), and malachite [$\text{Cu}_2(\text{OH})_2\text{CO}_3$]. However, 80% of the world copper production comes from the ore chalcopryrite (CuFeS_2). The extraction of copper from chalcopryrite involves partial roasting, removal of iron and self-reduction.

1. Partial roasting of chalcopryrite produces

- (1) Cu_2S and FeO (2) Cu_2O and FeO
 (3) Cu_2O and Fe_2O_3 (4) CuS and Fe_2O_3

2. Iron is removed from chalcopryrite as

- (1) FeO (2) FeS
 (3) Fe_2O_3 (4) FeSiO_3

3. In self-reduction, the reducing species is

- (1) S (2) O^{2-}
 (3) S^{2-} (4) SO_2

Paragraph 2

Extraction of copper is done using copper pyrites. After roasting, the ore is mixed with silica and coke and then smelted in a blast furnace. The matte obtained from the blast furnace is charged into a silica-lined converter. Some silica is also added, and a hot air blast is blown into the mixture to obtain blister copper, which is purified by electrorefining.

4. The chemical formula of copper pyrites is

- (1) CuFeS_2 (2) Cu_2O
 (3) Cu_2S (4) $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$

5. The chemical composition of the slag formed during smelting is

- (1) CuSiO_3 (2) FeSiO_3
 (3) CaSiO_3 (4) $\text{Cu}_2\text{O} \cdot \text{SiO}_2$

6. Coke is added during smelting to

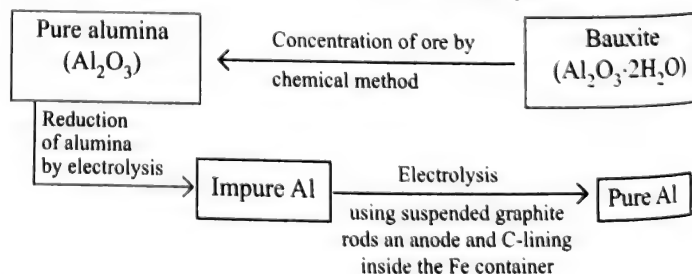
- (1) Reduce FeO to Fe
 (2) Reduce Cu_2O to Cu
 (3) Check the oxidation of FeO to Fe_2O_3
 (4) Check the oxidation of Cu_2O to CuO

7. Matte is a mixture of

- (1) $\text{Cu}_2\text{S} + \text{FeS}$ (small amount)
 (2) $\text{FeS} + \text{Cu}_2\text{S}$ (small amount)
 (3) $\text{Cu}_2\text{O} + \text{FeO}$ (small amount)
 (4) $\text{FeO} + \text{Cu}_2\text{S}$ (small amount)

Paragraph 3

Extraction of aluminium can be understood by:



Electrolytic reduction of Al_2O_3 :

Electrolyte: $\text{Al}_2\text{O}_3 + \text{Cryolite} + \text{CaF}_2$

Cathode: Carbon inside the Fe container

Anode: Graphite rods

Linked Comprehension Type

Paragraph 1

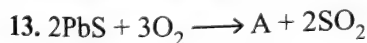
Copper is the most noble of first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), atacamite [$\text{Cu}_2\text{Cl}(\text{OH})_3$], cuprite

8. The purpose of adding cryolite is
- (1) To remove the impurities as slag
 - (2) To lower the melting point of Al_2O_3
 - (3) To decrease the electrical conductivity of pure aluminium
 - (4) To increase the Al percentage in the yield
9. Coke powder is spread over the molten electrolyte to
- (1) Prevent the corrosion of graphite anode
 - (2) Prevent the heat radiation from the surface
 - (3) Prevent the oxidation of molten aluminium by air
 - (4) Both (1) and (2)
10. The function of fluorspar (CaF_2) is
- (1) To increase the melting point of electrolyte
 - (2) To increase electrolytic conductivity power
 - (3) To remove the impurities as slag
 - (4) All of these
11. The molten electrolytes contain Na^+ , Al^{3+} and Ca^{2+} but only Al gets deposited at cathode because,
- (1) Standard reduction potential of Al is more than that of Na and Ca
 - (2) Standard oxidation potential of Al is more than that of Na and Ca
 - (3) Graphite reacts only with Al^{3+} and not with Na^+ and Ca^{2+}
 - (4) Discharge potential of Al^{3+} is higher than Na^+ and Ca^{2+}

Paragraph 4

Roasting is a process in which the ore (mostly sulphide) is heated strongly in the presence of excess of air. The heating should be done at a temperature below the melting point of the ore.

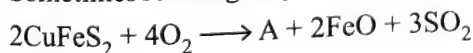
12. Select the correct statement:
- (1) Roasting removes easily oxidisable volatile impurities like arsenic as As_2O_3 , antimony as Sb_2O_3 , and sulphur as SO_2
 - (2) The release of SO_2 (in roasting process) has been a serious air pollution problem
 - (3) In roasting process, if temperature is fairly low (about 500°C) and the concentration of SO_2 in the gaseous environment is more, sulphate may be produced, that is stable, and high temperature is needed to decompose it
 - (4) All are correct



The name of A is

- (1) Litharge
- (2) Galena
- (3) Sesquioxide
- (4) None of these

14. Sometimes roasting may not bring about complete oxidation:



Find out A:

- (1) Cu_2O
- (2) CuO
- (3) Cu_2O
- (4) CuS

Paragraph 5

Lead obtained from galena (PbS) by air reduction or carbon reduction process contains base metal (Cu, Bi, Sn, As) as impurities, due to the which lead becomes hard and brittle.

15. Parke's process is also called

- (1) Softening process
 - (2) Desilverisation method
 - (3) Cupellation
 - (4) None of these
16. Cupellation is used for purification of
- (1) Pb
 - (2) Ag
 - (3) Zn
 - (4) Fe
17. Ag can be obtained from purified Zn-Ag alloy by
- (1) Distillation
 - (2) Poling
 - (3) Liquefaction
 - (4) Reduction

18. Zn-Ag alloy formed in the upper layer of molten lead is skimmed off from the surface of the molten lead by perforated ladles. This alloy contains lead as impurity. This impurity of Pb is removed by

- (1) Distillation
- (2) Cupellation
- (3) Liquefaction
- (4) Bett's electrolysis

Paragraph 6

Lead obtained from galena ore (PbS) by air reduction or carbon reduction process contains base metal (Cu, Bi, As, Sn, Zn) as impurities.

19. The removal of the impurity of Ag from the commercial lead is called

- (1) Desilverization of lead
- (2) Softening process
- (3) Bett's electrolysis
- (4) Cupellation

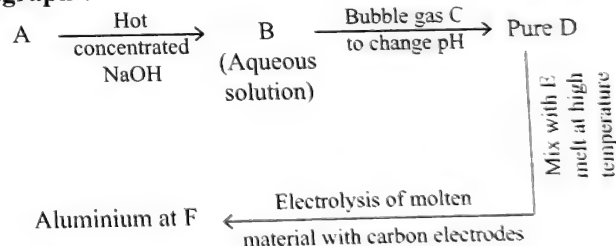
20. The electrolyte used for electrolysis of Pb is

- (1) $\text{PbSO}_4 + \text{H}_2\text{SO}_4$
- (2) $\text{PbCl}_2 + \text{HCl}$
- (3) $\text{PbSiF}_6 + \text{H}_2\text{SiF}_6$
- (4) None of these

21. Gelatin acts as addition agent in electrolysis of Pb. In the presence of gelatin, Pb becomes

- (1) Hard and brittle
- (2) Soft and useless
- (3) Smooth and uniform
- (4) Only brittle

Paragraph 7



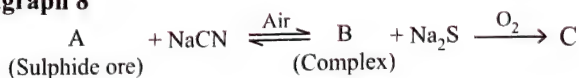
22. A is
- (1) CuFeS_2
 - (2) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
 - (3) $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
 - (4) CuS

23. B is:
- (1) $\text{Na}[\text{Al}(\text{OH})_4]$
 - (2) NaOH
 - (3) H_2SO_4
 - (4) Al_2O_3

24. C is
- (1) CO_2
 - (2) SO_2
 - (3) SO_3
 - (4) NO_2

25. E is
- (1) Na_3GeF_6
 - (2) Na_3AlF_6
 - (3) Al_2O_3
 - (4) None of these

26. F is
- (1) Cathode
 - (2) Anode
 - (3) Electrolyte
 - (4) None of these

Paragraph 8

27. A is

- (1) As_2S (2) CuS
(3) Na_2S (4) HgS

28. Composition of B is

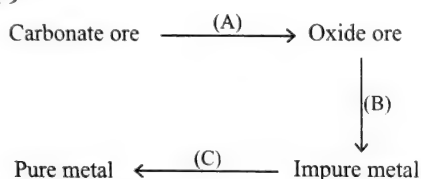
- (1) $\text{Na}[\text{Ag}(\text{CN})_2]$ (2) $\text{Na}_2[\text{Ag}(\text{CN})_2]$
(3) $\text{Na}[\text{Ag}(\text{CN})_4]$ (4) $\text{Na}_3[\text{Ag}(\text{CN})_2]$

29. B is

- (1) Ferromagnetic
(2) Paramagnetic
(3) Linear complex
(4) Coordination number of central atom is 4

30. C is

- (1) Na_2SO_4 (2) Na_2SO_3
(3) Na_2O (4) Na_2O_2

Paragraph 9

31. Name the process (A)

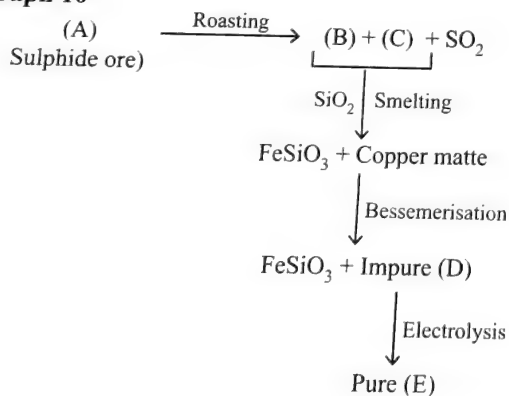
- (1) Roasting (2) Smelting
(3) Calcination (4) Reduction

32. Name the process (B)

- (1) Reduction (2) Roasting
(3) Mond's process (4) Van Arkel process

33. Name the process (C)

- (1) Reduction (2) Zone-refining
(3) Roasting (4) Calcination

Paragraph 10

34. Identify (A)

- (1) CuS (2) FeS_2
(3) CuFeS_2 (4) Fe_3O_4

35. Identify (B) and (C):

- (1) $\text{FeS} + \text{FeO}$ (2) $\text{FeO} + \text{Cu}_2\text{S}$
(3) $\text{FeS} + \text{Cu}_2\text{O}$ (4) $\text{Cu}_2\text{O} + \text{Cu}_2\text{S}$

36. Composition of copper matte is

- (1) $\text{Cu}_2\text{S} + \text{FeS}$ (small amount)
(2) $\text{Cu}_2\text{O} + \text{FeS}$ (small amount)
(3) $\text{Cu}_2\text{S} + \text{FeSO}_4$ (small amount)
(4) $\text{Cu}_2\text{S} + \text{FeO}$ (small amount)

37. Identify (E):

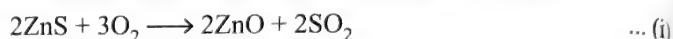
- (1) Blister Cu (2) Pig iron
(3) FeO (4) Wrought iron

38. Pure (E) is

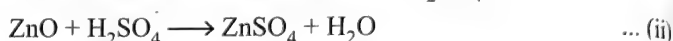
- (1) Cu (2) Fe
(3) S (4) O_2

Paragraph 11

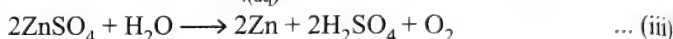
Chief ore of Zn is ZnS . The ore is concentrated by froth flotation process and then heated in air to convert ZnS to ZnO .



ZnO , thus formed is treated with dilute H_2SO_4 .



On electrolysis of $\text{ZnSO}_{4(\text{aq})}$, Zn metal is produced.



39. What mass of Zn will be obtained from an ore containing 225 kg of ZnS ? ($\text{Zn} = 65$, $\text{S} = 32$, $\text{O} = 16$, $\text{H} = 1$)

- (1) 102 kg (2) 151 kg
(3) 112 kg (4) 134 kg

40. ZnO on dissolution in NaOH gives

- (1) Na_2ZnO_2 (2) NaZnO_2
(3) $\text{NaZn}(\text{OH})_4$ (4) NaZn_2O_3

41. How many kilomoles of NaOH are required to dissolve all the ZnO produced in reaction (ii)?

- (1) 1.16 (2) 2.32
(3) 4.64 (4) 9.28

42. What volume of 98% H_2SO_4 (by weight, density = 1.8 g/mL) is required in step (ii)?

- (1) 120 L (2) 129 L
(3) 1.40 L (4) 150 L

Matrix Match Type

This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

Column I		Column II	
a.	Azurite	i.	Sulphide of iron
b.	Malachite	ii.	Sulphide of copper
c.	Chalcopyrites	iii.	Oxides of copper
d.	Cuprite	iv.	Ore containing carbonate of copper
e.	Magnesite	v.	Ore of magnesium
f.	Dolomite	vi.	Carbonate ore

2.

Column I		Column II	
a.	Iron pyrites	i.	Fe_2O_3
b.	Fool's gold	ii.	FeS_2
c.	Haematite	iii.	Sulphide ore
d.	Galena	iv.	Al_2O_3
e.	Corundum	v.	Concentrated by froth flotation process
f.	Bauxite	vi.	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$

3.

Column I		Column II	
a.	Mond's process	i.	Refining of Ag
b.	Thermite process	ii.	Extraction of Cr
c.	Poling	iii.	Refining of Cu
d.	Cupellation	iv.	Refining of Zr
e.	Van Arkel method	v.	Extraction and purification of Ni
f.	Carbon reduction method	vi.	Iron

4.

Column I		Column II	
a.	Diaspore	i.	Al_2O_3
b.	Bauxite	ii.	KNO_3
c.	Corundum	iii.	$\text{CaCO}_3 \cdot \text{MgCO}_3$
d.	Indian saltpetre	iv.	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
e.	Carnallite	v.	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
f.	Dolomite	vi.	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

5.

Column I		Column II	
a.	Mond's process	i.	Purification of Ge
b.	Van Arkel method	ii.	Purification of Ni

c.	Zone refining	iii.	Extraction of Au
d.	Polling	iv.	Purification of Ti
e.	Cupellation	v.	Refining of Ag
f.	Cyanide process	vi.	Purification of copper

6.

Column I		Column II	
a.	Gypsum	i.	Hg
b.	Cinnabar	ii.	Pb
c.	Galena	iii.	Ca
d.	Argentite	iv.	Al
e.	Corundum	v.	Mg
f.	Carnallite	iv.	Ag

7.

Column I		Column II	
a.	Copper pyrites	i.	Fluoride ore
b.	Cryolite	ii.	Sulphate ore
c.	Rock salt	iii.	Oxide ore
d.	Alumina	iv.	Sulphide ore
e.	Dolomite	v.	Chloride ore
f.	Gypsum	vi.	Carbonate ore

8.

Column I		Column II	
a.	Chile saltpetre	i.	Mg
b.	Pyrolusite	ii.	Pb
c.	Kiesserite	iii.	Be
d.	Anglesite	iv.	Na
e.	Beryl	v.	Mn
f.	Rutile	vi.	Ti

9. Match the items given in Column I with that in Column II and III

Column I		Column II		Column III	
a.	Froth floatation method	i.	Used to separate ZnS and PbS	p.	The crude metal is heated in evacuated vessel with I_2 . The metal iodide is decomposed on electrically heating to give pure metal
b.	Depressants	ii.	Method is based on the principle that the impurities are more soluble in the melt than in solid state of metal	q.	Used for removing gangue from sulphide ores
c.	Zone refining method	iii.	Collectors (like pine oils, fatty acids) and stabilisers (like, aniline, cresols) are added	r.	NaCN is added
d.	van Arkel method	iv.	This method is used to remove all O_2 and N_2 present in the form of impurity in metals like Zr and Ti	s.	Method is useful for producing semiconductors of high purity, eg; Ge, Si, B, Ga and In

For Q. 10 to Q. 13:

Answer the questions given below by appropriately matching the information given in three Column of the following table.

Column I		Column II		Column III	
Metals		Occurrence		Common method of Extraction	
a.	Zn	i.	Haematite	p.	Roasting followed by reduction with coke. The metal may be purified by fractional distillation
b.	Cu	ii.	Calamine	q.	Roasting of sulphide ore partially and reduction. It is self reduction in a specially designed converter. H_2SO_4 leaching is also used in hydrometallurgy from low grade ores
c.	Fe	iii.	Cryolite	r.	Electrolysis of oxide ore dissolved in molten salt. Good source of electricity is required
d.	Al	iv.	Malachite	s.	Reduction of the oxide with CO and coke in Blast furnace at 2170 K.

10. For the ore SPHALERITE, CORRECT combination is:

- (1) a-ii-p (2) b-iv-q
(3) c-i-s (4) d-iii-r

11. For the ore MAGNETITE, CORRECT combination is:

- (1) a-ii-p (2) b-iv-q
(3) c-i-s (4) d-iii-r

12. For the ore BAUXITE, CORRECT combination is:

- (1) a-ii-p (2) d-iii-r
(3) b-iv-q (4) c-i-s

13. For the ore COPPER PYRITES, CORRECT combination is:

- (1) a-ii-p (2) b-iv-q
(3) c-i-s (4) b-iv-q

10. How many of the following are oxide ores

Calamine, cuprite, zincite, chalcocite, haematite, bauxite, magnetite, cassiterite

11. How many ores are sulphide ores from the given ores?
Azurite, chalcite, iron pyrites, limonite

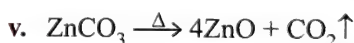
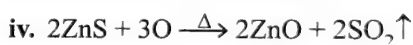
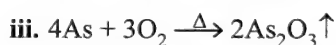
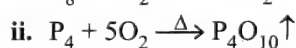
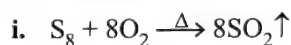
12. How many metals are commercially purified by Van Arkel method from the given metals?

Ti, B, Zr, Pb, Hg

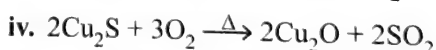
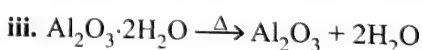
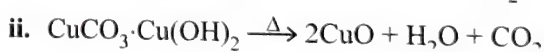
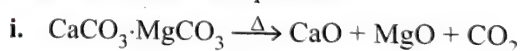
13. How many metals are commercially purified by electrolysis method from the given metals?

Na, Al, Pb, Ni

14. Find the number of following reactions which are involved in roasting process:



15. Find the number of reaction from the given reactions which can show calcination process:



16. How many metallic ores are concentrated by magnetic separation method from the given ores?

Cassiterite, pyrolusite, rutile, magnetite, galena, cinnabar.

17. Find the number of metal oxides which are decomposed on normal heating from the given oxides:

 Na_2O , Al_2O_3 , PbO , Ag_2O , HgO

18. Find the number of basic flux from the given compounds:

 SiO_2 , MgO , CaO , FeO , B_2O_3 , CaCO_3

19. Find the number of metals from the given metals which can be commercially purified by zone refining methods:

Si, Ge, Ga, Al, Ti, Zr

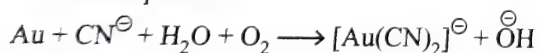
Numerical Value Type

1. In the bauxite ore, what is the value of x ?

2. Carnallite consists of how many different compounds?

3. In Goldschmidt's aluminothermic process, thermite mixture contains _____ parts of Fe_2O_3 and one part of aluminium.4. What is the value of x in $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$, gypsum?

5. How many cyanide ions are involved in the following chemical equation?



6. How many of the following metals can be refined by vapour phase refining?

Zn, Zr, Hg, Cd, Ni, Ti, Co, Pt, Fe

7. Amongst the following elements, how many occurs in the earth's crust in the native state?

Au, Pt, Hg, Zn, Fe

8. Amongst the following, how many ores can be concentrated by froth flotation process:

Galena, sphalerite, cassiterite, calamine, chalcocite, haematite, argente

9. Amongst the following, how many ores are roasted to convert them into their corresponding metal oxides, alumina, zinc blende, iron pyrites, copper pyrites, galena.

20. How many metals are commercially extracted by pyrometallurgy from the given metal?
Cu, Fe, Sn, Au, K, Na
21. Find the number of acidic flux from the given compounds:
 CaCO_3 , $\text{Na}_2\text{B}_4\text{O}_7$, MgSiO_3 , FeSiO_3 , P_2O_5
22. How many reactions can show slag formation process from the given reactions?
i. $\text{SiO}_2 + \text{CaO} \longrightarrow \text{CaSiO}_3$
ii. $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$
iii. $\text{CaO} + \text{P}_2\text{O}_5 \longrightarrow \text{Ca}_3(\text{PO}_4)_2$
iv. $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$
v. $\text{MgCO}_3 + \text{SiO}_2 \longrightarrow \text{MgSiO}_3 + \text{CO}_2$
23. How many metals are commercially extracted by electro-metallurgy from the given metals?
Al, Mg, Na, K, Ag, Hg, Ti, Th, Zr, B
24. How many metals are commercially extracted by hydrometallurgy from the given metals:
Ag, Mn, In, Cr, Pb, Au
25. How many metals are commercially reduced by Goldschmidt's aluminothermic process from the given metals?
Na, Pb, Al, Mn, Sn
26. Find the number of metals which are commercially reduced by self-reduction from the given metals:
Fe, Al, Zn, Sn, Pb, Hg, Cu
27. Find the number of metals which are commercially reduced by carbon reduction method from the given metals:
Ag, Cr, Mn, Sn, Zn, Fe

Archives

JEE MAIN

Single Correct Answer Type

1. Mond's process is used for preparing
(1) Ni (2) H_2SO_4
(3) NH_3 (4) HNO_3 (AIEEE 2010)
2. Gold is extracted by hydrometallurgical process based on its property
(1) of being electropositive
(2) of being less reactive
(3) to form complexes which are water soluble
(4) to form salts which are water soluble (AIEEE 2012)
3. Roasting of sulphides gives the gas X as a by-product. This is a colorless gas produce choking smell of burnt sulphur, and causes great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic and acts as a reducing agent and it has never been isolated. The gas X is
(1) SO_2 (2) CO_2
(3) SO_3 (4) H_2S (JEE Main 2013)
4. In the context of the Hall-Heroult process for the extraction of Al, which of the following statements is false?
(1) CO and CO_2 are produced in this process
(2) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivity
(3) Al^{3+} is reduced at the cathode to form Al
(4) Na_3AlF_6 serves as the electrolyte (JEE Main 2015)
5. Which one of the following ores is best concentrated by froth floatation method?
(1) Malachite (2) Magnetite
(3) Siderite (4) Galena (JEE Main 2016)

6. When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is

- (1) Ca (2) Al
(3) Fe (4) Zn (JEE Main 2018)

JEE ADVANCED

Single Correct Answer Type

1. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are
(1) II, III in haematite and III in magnetite
(2) II, III in haematite and II in magnetite
(3) II in haematite and II, III in magnetite
(4) III in haematite and II, III in magnetite (IIT-JEE 2011)
2. Sulfide ores are common for the metals.
(1) Ag, Cu and Pb (2) Ag, Cu and Sn
(3) Ag, Mg and Pb (4) Al, Cu and Pb (JEE Advanced 2013)
3. Which series of reactions correctly chemical reactions related to iron and its compound
- (1) $\text{Fe} \xrightarrow{\text{Cl}_2, \text{heat}} \text{FeCl}_3 \xrightarrow{\text{heat, air}} \text{FeCl}_2 \xrightarrow{\text{Zn}} \text{Fe}$
- (2) $\text{Fe} \xrightarrow{\text{O}_2, \text{heat}} \text{Fe}_3\text{O}_4 \xrightarrow{\text{CO}, 600^\circ\text{C}} \text{FeCl}_2 \xrightarrow{\text{CO}, 700^\circ\text{C}} \text{Fe}$
- (3) $\text{Fe} \xrightarrow{\text{dil. H}_2\text{SO}_4} \text{FeSO}_4 \xrightarrow{\text{H}_2\text{SO}_4, \text{O}_2} \text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\text{heat}} \text{Fe}$
- (4) $\text{Fe} \xrightarrow{\text{O}_2, \text{heat}} \text{FeO} \xrightarrow{\text{dil. H}_2\text{SO}_4} \text{FeSO}_4 \xrightarrow{\text{heat}} \text{Fe}$ (JEE Advanced 2014)

Multiple Correct Answers Type

1. Extraction of metal from the ore cassiterite involves
 (1) Carbon reduction of an oxide ore
 (2) Self-reduction of sulphide ore
 (3) Removal of copper impurity
 (4) Removal of iron impurity (IIT-JEE 2011)

2. The carbon-based reduction method is **NOT** used for the extraction of

- (1) Tin from SnO_2
 (2) Iron from Fe_2O_3
 (3) Aluminium from Al_2O_3
 (4) Magnesium from $\text{MgCO}_3 \cdot \text{CaCO}_3$

(JEE Advanced 2013)

3. Upon heating with Cu_2S , the reagent(s) that give copper metal is/are

- (1) CuFeS_2 (2) CuO
 (3) Cu_2O (4) CuSO_4

(JEE Advanced 2014)

4. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is (are)

- (1) Impure Cu strip is used as cathode
 (2) Acidified aqueous CuSO_4 is used as electrolyte
 (3) Pure Cu deposits at cathode
 (4) Impurities settle as anode-mud

(JEE Advanced 2015)

5. Extraction of copper from copper pyrite (CuFeS_2) involves

- (1) crushing followed by concentration of the ore by froth-flotation
 (2) removal of iron as slag
 (3) self-reduction step to produce 'blistercopper' following evolution of SO_2
 (4) refining of 'blister copper' by carbon reduction

(JEE Advanced 2016)

Linked Comprehension Type**Problems 1–3**

Copper is the most noble of the first row transition elements. It occurs in small deposits in several countries. Ores of copper include chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), atacamite [$\text{Cu}_2\text{Cl}(\text{OH})_3$], cuprite (Cu_2O), copper glance (Cu_2S), and malachite [$\text{Cu}_2(\text{OH})_2\text{CO}_3$]. However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS_2). Extraction of copper from chalcopyrite includes roasting, iron removal, and self-reduction.

1. Partial roasting of chalcopyrite produces

- (1) Cu_2S and FeO (2) Cu_2O and FeO
 (3) CuS and Fe_2O_3 (4) Cu_2O and Fe_2O_3

2. Iron is removed from chalcopyrite as

- (1) FeO (2) FeS
 (3) Fe_2O_3 (4) FeSiO_3

3. In self-reduction, the reducing species is

- (1) S (2) O^{2-}
 (3) S^{2-} (4) SO_2

(IIT-JEE 2010)

Matrix Match Type

1. Match the extraction processes listed in Column I with the metals listed in Column II.

Column I		Column II	
a.	Self-reduction	p.	Lead
b.	Carbon reduction	q.	Silver
c.	Complex formation and displacement by metal	r.	Copper
d.	Decomposition of iodide	s.	Boron

(IIT-JEE 2006)

2. Match the conversions in Column I with the type(s) of reaction(s) given in Column II.

Column I		Column II	
a.	$\text{PbS} \longrightarrow \text{PbO}$	p.	Roasting
b.	$\text{CaCO}_3 \longrightarrow \text{CaO}$	q.	Calcination
c.	$\text{ZnS} \longrightarrow \text{Zn}$	r.	Carbon reduction
d.	$\text{Cu}_2\text{S} \longrightarrow \text{Cu}$	s.	Self-reduction

(IIT-JEE 2008)

3. Match the anionic species given in Column I that are present in the ore(s) given in Column II.

Column I		Column II	
a.	Carbonate	p.	Siderite
b.	Sulphide	q.	Malachite
c.	Hydroxide	r.	Bauxite
d.	Oxide	s.	Calamine
		t.	Argentite

(JEE Advanced 2015)

Numerical Value Type

1. Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the contents undergo self-reduction. The weight (in kg) of Pb produced per kg of O_2 consumed is _____.

(JEE Advanced 2018)

Answers Key

EXERCISES

Single Correct Answer Type

1. (1) 2. (3) 3. (2) 4. (3) 5. (1)
6. (2) 7. (1) 8. (1) 9. (3) 10. (4)
11. (1) 12. (4) 13. (3) 14. (3) 15. (2)
16. (1) 17. (3) 18. (2) 19. (3) 20. (1)
21. (1) 22. (4) 23. (2) 24. (2) 25. (4)
26. (3) 27. (2) 28. (3) 29. (1) 30. (2)
31. (4) 32. (2) 33. (3) 34. (3) 35. (4)
36. (2) 37. (2) 38. (3) 39. (4) 40. (2)
41. (4) 42. (1) 43. (1) 44. (2) 45. (2)
46. (2) 47. (2) 48. (2) 49. (4) 50. (2)
51. (4) 52. (3) 53. (1) 54. (4) 55. (4)
56. (4) 57. (1) 58. (4) 59. (4) 60. (3)
61. (2) 62. (1) 63. (1) 64. (3) 65. (3)
66. (1) 67. (1) 68. (3) 69. (4) 70. (4)
71. (3) 72. (2) 73. (1) 74. (2) 75. (1)
76. (2) 77. (2) 78. (2) 79. (1) 80. (2)
81. (2) 82. (3) 83. (1) 84. (1) 85. (1)
86. (3) 87. (4) 88. (2) 89. (3) 90. (1)
91. (1) 92. (4) 93. (4) 94. (2) 95. (3)
96. (1) 97. (1) 98. (1) 99. (3) 100. (1)
101. (1) 102. (1) 103. (4) 104. (1) 105. (3)
106. (1) 107. (3) 108. (1) 109. (4) 110. (2)
111. (4) 112. (2) 113. (4) 114. (4) 115. (3)
116. (2) 117. (2) 118. (1) 119. (2) 120. (1)
121. (1) 122. (2) 123. (2) 124. (2) 125. (2)
126. (3) 127. (3) 128. (1) 129. (3) 130. (1)
131. (4) 132. (1) 133. (4) 134. (2) 135. (4)
136. (4) 137. (3) 138. (3) 139. (2) 140. (2)
141. (4) 142. (1) 143. (3)

Multiple Correct Answers Type

1. (1, 2, 3) 2. (1, 2, 4) 3. (1, 2, 3)
4. (2, 3, 4) 5. (2, 3) 6. (3, 4)
7. (1, 2) 8. (1, 3) 9. (1, 2, 3)
10. (2, 3, 4) 11. (1, 2, 3, 4) 12. (2, 3, 4)
13. (1, 2) 14. (1, 2, 4) 15. (1, 2, 3)
16. (1, 2, 3, 4) 17. (2, 4) 18. (1, 2)
19. (1, 2) 20. (1, 2, 3) 21. (1, 3)
22. (1, 2, 3, 4) 23. (1, 3) 24. (1, 2, 3)
25. (1, 2) 26. (1, 2) 27. (2, 3, 4)
28. (1, 3, 4) 29. (1, 3) 30. (1, 2, 3)
31. (1, 2, 3) 32. (2, 3, 4) 33. (1, 2)
34. (3, 4) 35. (1, 2, 3) 36. (2, 4)
37. (3, 4) 38. (1, 2) 39. (1, 2, 3)
40. (1, 3, 4) 41. (2, 3, 4) 42. (1, 2, 4)
43. (1, 3, 4) 44. (1, 2, 3) 45. (1, 2)
46. (2, 4) 47. (1, 2) 48. (1, 3, 4)
49. (2, 4) 50. (1, 3) 51. (2, 3)
52. (4) 53. (1, 2, 3, 4) 54. (1, 2, 3)

55. (1, 4)

58. (1, 2, 4)

56. (1, 2, 4)

59. (2, 3)

57. (1, 4)

60. (1, 4)

Linked Comprehension Type

1. (1) 2. (4) 3. (3) 4. (1) 5. (1)
6. (3) 7. (1) 8. (2) 9. (4) 10. (2)
11. (1) 12. (4) 13. (1) 14. (3) 15. (2)
16. (2) 17. (1) 18. (3) 19. (1) 20. (3)
21. (3) 22. (3) 23. (1) 24. (1) 25. (2)
26. (1) 27. (1) 28. (1) 29. (2, 3) 30. (1)
31. (3) 32. (2) 33. (2) 34. (3) 35. (2)
36. (1) 37. (1) 38. (1) 39. (2) 40. (1)
41. (1) 42. (2)

Matrix Match Type

Q. No.	a	b	c	d	e	f
1.	iv	iv	i, ii	ii	vi	v
2.	ii	ii, iii	i	v	iv	vi
3.	v	ii	iii	i	iv	vi
4.	vi	v	i	ii	vi	iii
5.	ii	iv	i	vi	v	iii
6	iii	i	ii	vi	iv	v
7	iv	i	v	iii	vi	ii
8.	iv	v	i	ii	vi	iii
9.	iii-q	i-r	ii-s	iv-p		

10. (1)

11. (3)

12. (2)

13. (4)

Numerical Value Type

1. (2) 2. (3) 3. (3) 4. (2) 5. (8)
6. (3) 7. (2) 8. (3) 9. (4) 10. (6)
11. (2) 12. (3) 13. (3) 14. (4) 15. (3)
16. (4) 17. (2) 18. (4) 19. (3) 20. (3)
21. (2) 22. (4) 23. (4) 24. (2) 25. (2)
26. (4) 27. (3)

ARCHIVES

JEE Main

Single Correct Answer Type

1. (1) 2. (3) 3. (1) 4. (4) 5. (4)
6. (2)

JEE Advanced

Single Correct Answer Type

1. (4) 2. (1) 3. (2)

Multiple Correct Answers Type

1. (1, 4) 2. (3, 4) 3. (3)
4. (2, 3, 4) 5. (1, 2, 3)

Linked Comprehension Type

1. (1) 2. (4) 3. (3)

Matrix Match Type

1. (a. \rightarrow p., r.; b. \rightarrow p.; c. \rightarrow q.; d. \rightarrow s.)
2. (a. \rightarrow p.; b. \rightarrow q.; c. \rightarrow p., r.; d. \rightarrow p., s.)
3. (a. \rightarrow p., q., s.; b. \rightarrow t.; c. \rightarrow q., r.; d. \rightarrow r.)

Numerical Value Type

1. 6.74 kg

2

p-Block Group 15 Elements The Nitrogen Family

OVERVIEW

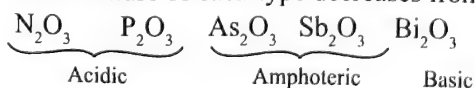
- Group 15 elements of the periodic table are collectively known as pnictogens.
- The general electronic configuration of elements of group 15 is $ns^2 np^3$.
- Gradation in atomic and physical properties
 - Covalent radii:** $N < P < As < Sb < Bi$
 - Ionisation energy (IE):** $N > P > As > Sb > Bi$
 - Electronegativity (EN):** $N > P > As > Sb > Bi$
 - Melting point/K:** $N < P < Bi < Sb < As$
 - Boiling point/K:** $P < N < As < Bi < Sb$
 - Density:** $N < P < As < Sb < Bi$
- Nitrogen exists as a diatomic inert gas whereas others exist in tetrahedral tetraatomic forms P_4 , As_4 , Sb_4 and are solids.
- Metallic nature increases down the group.

N	P	As	Sb	Bi
Non-metals		Metalloids		Metal
- Due to inert pair effect, group 15 elements show variable oxidation states of -3, +3 and +5. Stability of +5 oxidation state decreases down the group. Nitrogen besides -3, +3 and +5 oxidation states, also shows -2, -1, 0, +1, +2 and +4 oxidation states in its oxides.
- Nitrogen shows maximum covalency of 4, whereas others can expand their covalency to 5 or 6 due to the presence of vacant d -orbitals in their valence shell.
- Only nitrogen is capable of forming $p\pi-p\pi$ multiple bonds with itself and with carbon, oxygen etc. due to compatibility in size and high extent of overlap of orbitals. Phosphorous and other members do not form $p\pi-p\pi$ multiple bond but are capable of forming $p\pi-d\pi$ bond.
- Group 15 elements form hydrides of type, EH_3

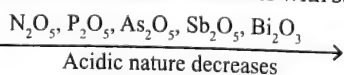
Bond angle: $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Acidic character: $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

Reducing agent: $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
- Oxides of type X_2O_3 , X_2O_4 and X_2O_5 are formed by the elements of group 15.
 - Greater is the electronegativity more is the acidic nature of its oxides.
 - Acidic nature of each type decreases from N to Bi.



However, it shows feeble acidic character with strong alkali.



Acidic nature of M_2O_4 oxides also decreases from N_2O_4 to Bi_2O_4 .

- Thermal stability decreases in each series from N to Bi.
 - In the oxides of a particular element, the acidic nature increases as the percentage of oxygen increases or the oxidation state increases.
- All the members of group 15 form oxyacids or oxoacids. The strength and stability of oxoacids having the element in same oxidation state decreases down the group.
 - Except nitrogen, the rest of the elements of group 15 form two series of halides EX_3 and EX_5 . Nitrogen does not form pentahalides due to absence of d -orbitals in its valence shell.
 - With the exception of N, all other group 15 elements form sulphides.
 - For drying NH_3 , quicklime (CaO) is used. Other dehydrating agents like H_2SO_4 , $CaCl_2$, P_2O_5 cannot be used as they react with NH_3 .
 - Nitrogen forms five oxides:**
 N_2O , NO , N_2O_3 , NO_2 or N_2O_4 and N_2O_5
 - HNO_3 also known as **aqua fortis** (meaning strong water) acts as monobasic acid. Noble metals like Au, Pt etc. dissolve in aqua regia i.e. $[3HCl (conc.) + 1 HNO_3 (conc.)]$
 - Proteins react with HNO_3 to form a yellow compound called xanthoprotein.
 - HNO_3 is used in manufacturing of explosives like TNT, picric acid, nitroglycerine etc.
 - Phosphoric exists in number of allotropic forms. Important ones are white or yellow phosphorous, red phosphorous and black phosphorous. White phosphorous is the most reactive allotrope.
 - Persons working with phosphorous develop a disease known as **phossy jaw**.
 - Some of the important compounds of group 15 are as follows:

i. Scheele's green	$CuHAsO_3$
ii. Graham salt	$(NaPO_3)_6$
iii. Paris green	$(CH_3COO)_2Cu \cdot 3Cu(AsO_2)_2$
iv. Pearl white	$BiOCl$
v. Nitrophosphate	$Ca(H_2PO_2)_2 + 2Ca(NO_3)_2$
vi. Superphosphate of lime	$Ca(H_2PO_4)_2 \cdot H_2O + 2CaSO_4 \cdot 2H_2O$
vii. Thomas slag	$2Ca_3(PO_4)_2 \cdot CaSiO_3$

- viii. Sindri fertilizer $(\text{NH}_4)_2\text{SO}_4$
 ix. Nangal fertilizer (CAN) $\text{Ca}(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3$
 x. Amatol $80\% \text{NH}_4\text{NO}_3 + 20\% \text{T.N.T.}$
 xi. Ammonal $\text{NH}_4\text{NO}_3 + \text{Al powder}$
 (small quantity)
 xii. Swarts reagent SbF_3
 xiii. Tartaremetic (Potassium antimonyl tartarate)
 xiv. Angelis salt $\text{Na}_2\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$

22. a. Radioactive phosphorous (^{32}P) is used in the treatment of leukemia.
 b. In toothpaste, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ is added as a mild abrasive and polishing agent.
 c. Amatol is $80\% \text{NH}_4\text{NO}_3 + 20\% \text{TNT}$ and is used as an explosive.

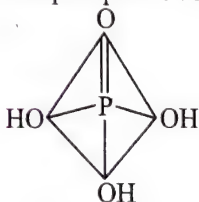
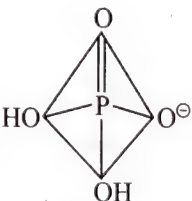
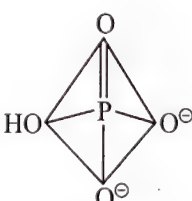
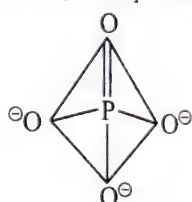
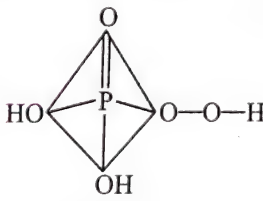
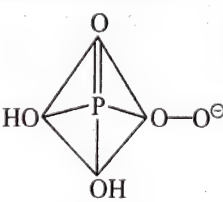
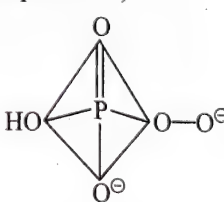
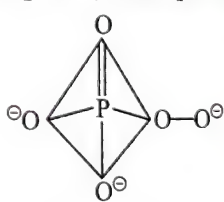
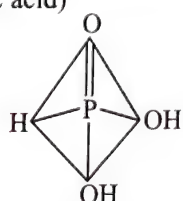
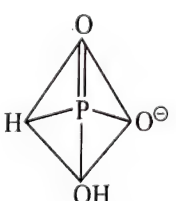
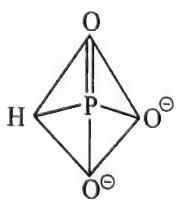
- d. P_4S_3 is used in matches. The head of the safety match box contains KClO_3 , KNO_3 or red lead along with grounded glass pieces and antimony sulphide. Sides of match box contain red phosphorous and sand powder.

23. Some examples of hybridisation of group 15 ($5e^-$)

Symbols used: SN = Steric number, lp = lone pair, bp = bond pair, H = hybridisation, G = Geometry, S = Shape, T.H. = Tetrahedron, Tbp = Trigonal bipyramid, O.H. = Octahedral, Pbp = Pentagonal bipyramid, T.E. = Transition elements, C.N. = Coordination number, V = No. of valence e^- 's, M = No. of monovalent atom attached to central atom, O.S. = Oxidation state, (e) = equatorial bond, (a) = axial bond.

Note: Oxoacids and peroxyacids and their ions have same hybridisation, geometry and shape.

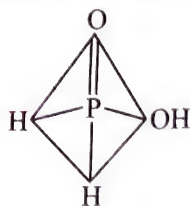
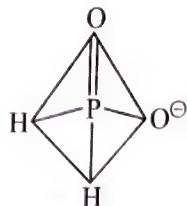
OXOACIDS OF PHOSPHOROUS

1.	H_3PO_4 (Tribasic acid) (O.S. = +5) (Phosphoric acid) or (orthophosphoric acid)  (a) $\mu \neq 0$ (P—O) Bond order = 1.5 $H = \frac{1}{2}(V+M) = \frac{1}{2}(5+3) = 4$	H_2PO_4^- (Dihydrogen phosphate ion)  (b) $\mu \neq 0$ SN = 4 bp	HPO_4^{2-} (Hydrogen phosphate)  (c) $\mu \neq 0$ H = sp^3	PO_4^{3-} (Phosphate ion) [One (p π -d π) multiple bond]  (d) $\mu \neq 0$ Due to four equivalent resonance structures Geometry = T.H., $109^\circ, 28'$
2.	H_3PO_5 (O.S. = +5) (Peroxyphosphoric acid) or (Perphosphoric acid)  (a) $\mu \neq 0$ $H = \frac{1}{2}(V+M) = \frac{1}{2}(5+3) = 4$	H_2PO_5^- (Dihydrogen-peroxyphosphate ion)  (b) $\mu \neq 0$ SN = 4 bp	HPO_5^{2-} (Hydrogen-peroxyphosphate ion)  (c) $\mu \neq 0$ H = sp^3	PO_5^{3-} (Peroxyphosphate ion) [One (p π -d π) multiple bond]  (d) $\mu \neq 0$ Geometry = T.H., $109^\circ, 28'$
3.	H_3PO_3 (Dibasic acid) (O.S. = +3) (Phosphorous acid) or (Phosphoric acid)  (a) $\mu \neq 0$ $H = \frac{1}{2}(V+M) = \frac{1}{2}(5+3) = 4$ (P—O) Bond order = 1.5	H_2PO_3^- (Dihydrogen phosphite ion)  (b) $\mu \neq 0$ SN = 4 bp	HPO_3^{2-} (Hydrogen phosphite ion)  (c) $\mu \neq 0$ H = sp^3	[One (p π -d π) multiple bond] Geometry = T.H., $109^\circ, 28'$

[One (pπ-dπ) multiple bond]

4. H_3PO_2 (Monobasic acid)
(O.S. = +1)
(Hypophosphorous acid)
or (Phosphenic acid)

H_2PO_2^-
(Dihydrogen hypophosphite
ion)

(a) $\mu \neq 0$ (b) $\mu \neq 0$

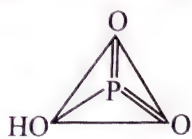
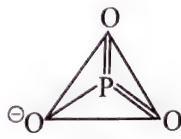
$$H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4 \quad \text{SN} = 4 \text{ bp}, H = sp^3,$$

G = T.H. $109^\circ, 28'$

(P—O) Band order = 1.5

5. HPO_3 (Monobasic acid)
(O.S. = +5)
(Metaphosphoric acid)

PO_3^-
(Metaphosphate ion)

(a) $\mu \neq 0$ 

(b)

(Due to three equivalent resonance structures)

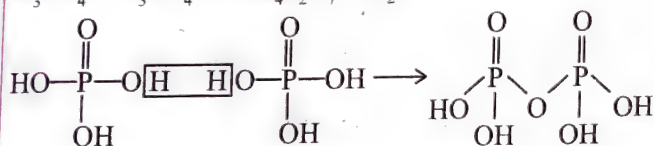
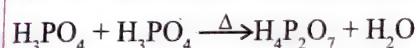
($\mu = 0$)

$$H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 1) = 3 \quad \text{SN} = 3 \text{ bp}, H = sp^2,$$

G = Planar 120°

[One (pπ-dπ) multiple bond]

6. Pyrophosphoric acid or diphosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$, tetrabasic acid, O.S. = +5)



$\text{H}_4\text{P}_2\text{O}_7$,
Pyrophosphoric acid (a)

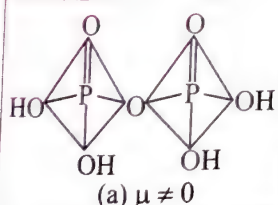
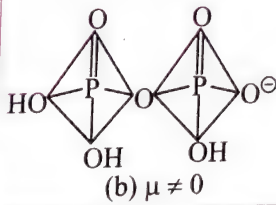
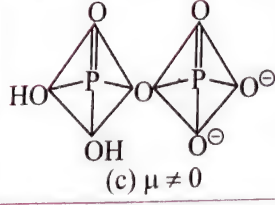
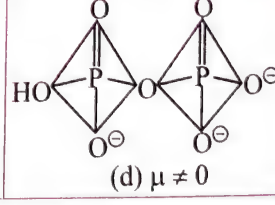
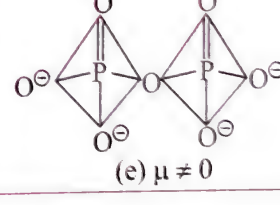
$\text{H}_3\text{P}_2\text{O}_7^-$
Trihydrogen-
pyrophosphate ion (b)

$\text{H}_2\text{P}_2\text{O}_7^{2-}$
Dihydrogen-pyrophos-
phate ion (c)

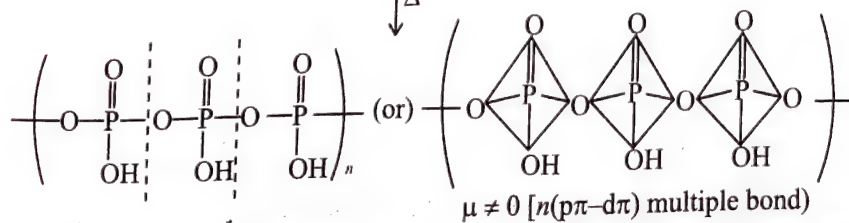
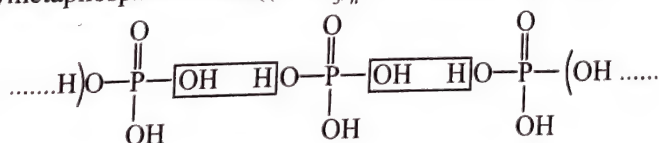
$\text{HP}_2\text{O}_7^{3-}$
Hydrogen-pyrophos-
phate ion (d)

$\text{P}_2\text{O}_7^{4-}$
Pyrophosphate
ion (e)

$$H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4 \quad \text{SN} = 4 \text{ bp}, H = sp^3, \text{ Geometry} = \text{T.H.}, 109^\circ, 28', [2 (\text{p}\pi\text{-d}\pi) \text{ multiple bond}]$$

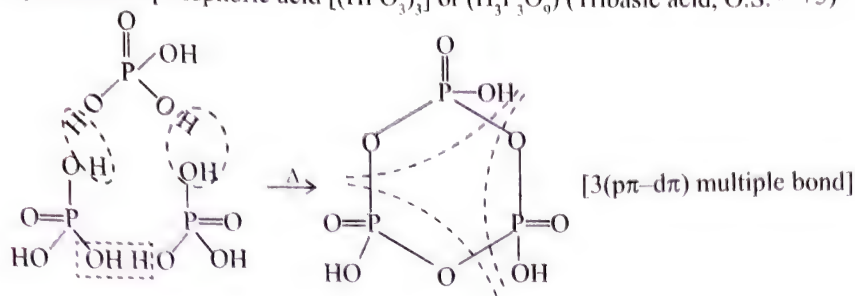
(a) $\mu \neq 0$ (b) $\mu \neq 0$ (c) $\mu \neq 0$ (d) $\mu \neq 0$ (e) $\mu \neq 0$

7. Polymetaphosphoric acid ($(\text{HPO}_3)_n$, Polybasic acid, O.S. = +5)

 $\mu \neq 0$ [$n(\text{p}\pi\text{-d}\pi)$ multiple bond]

$$H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4 \quad \text{SN} = 4 \text{ bp}, H = sp^3, \text{ Geometry} = \text{T.H.}, 109^\circ, 28'$$

8. Cyclotrimeta phosphoric acid $[(\text{HPO}_3)_3]$ or $(\text{H}_3\text{P}_3\text{O}_9)$ (Tribasic acid, O.S. = +5)



$\text{H}_3\text{P}_3\text{O}_9$
Cyclotrimeta-
phosphoric acid

$\text{H}_2\text{P}_3\text{O}_9^-$
Dihydrogen-
cyclotrimeta phos-
phate ion

$\text{HP}_3\text{O}_9^{2-}$
Hydrogen cyclotrimeta-
phosphate ion

$\text{P}_3\text{O}_9^{3-}$
Cyclotrimeta phosphate
ion

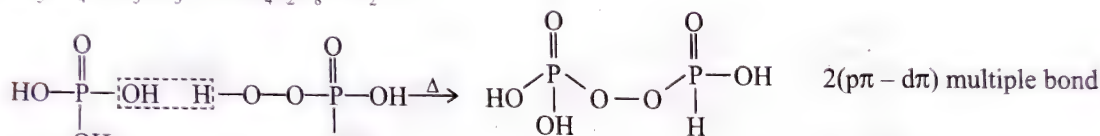
$$H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4$$

SN = 4 bp,

H = sp^3 ,

Geometry = T.H., $109^\circ, 28^\circ$

9. Perdiphosphoric acid $(\text{H}_4\text{P}_2\text{O}_8)$, Tetrabasic, O.S. = +5)



$\text{H}_4\text{P}_2\text{O}_8$
Perdiphosphoric
acid

$\text{H}_3\text{P}_2\text{O}_8^-$
Trihydrogen-
perdiphosphate ion

$\text{H}_2\text{P}_2\text{O}_8^{2-}$
Dihydrogen perdisphos-
phate ion

$\text{HP}_2\text{O}_8^{3-}$
Hydrogen perdisphos-
phate ion

$\text{P}_2\text{O}_8^{4-}$
Perdiphosphate ion

$$H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4$$

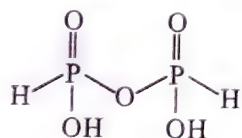
SN = 4 bp,

H = sp^3 ,

Geometry = T.H., $109^\circ, 28^\circ$

10. Pyrophosphorous acid $(\text{H}_4\text{P}_2\text{O}_5)$ (Dibasic, O.S. = +3)

$2(p\pi - d\pi)$ multiple bond



$\text{H}_3\text{P}_2\text{O}_5^-$
Trihydropyro-
phosphite ion

$\text{H}_2\text{P}_2\text{O}_5^{2-}$
Dihydropyro-
phosphite ion

$$H = \frac{1}{2}(V + M) = (5 + 3) = 4$$

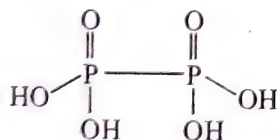
SN = 4 bp,

H = sp^3 ,

Geometry = T.H.,

11. Hypophosphoric acid $(\text{H}_4\text{P}_2\text{O}_6)$ (Tetrabasic, O.S. = +4)

$2(p\pi - d\pi)$ multiple bond



$\text{H}_3\text{P}_2\text{O}_6^-$
Trihydrohypo-
phosphate ion

$\text{H}_2\text{P}_2\text{O}_6^{2-}$
Dihydrohypo-
phosphate ion

$\text{HP}_2\text{O}_6^{3-}$
Hydrohypo-
phosphate ion

$\text{P}_2\text{O}_6^{4-}$
Hypophosphate ion

$$H = \frac{1}{2}(V + M) = (5 + 3) = 4$$

SN = 4 bp,

H = sp^3 ,

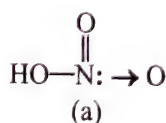
Geometry = T.H.

(P—O) bond order = 1.5

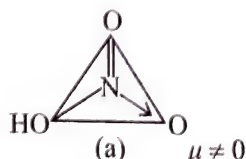
12. HNO_3 (nitric acid, monobasic, O.S. = +5)

NO_3^- nitrate ion
(or)

N atom does not have
d-orbitals. So [one $(p\pi - \pi\pi)$ multiple bond]

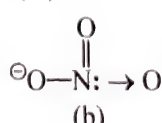


(a)

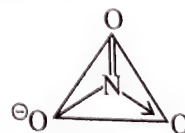


(a)

$\mu \neq 0$



(b)



(b)

$\mu \neq 0$

$$H = \frac{1}{2}(V + M) = (5 + 1) = 3$$

SN = 3 bp,

H = sp^2 ,

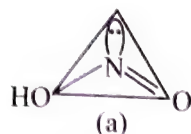
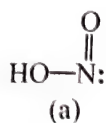
Geometry = Planar 120°

13. HNO_3 does not form per-oxy acid because its peroxy form having two central atom is not possible.

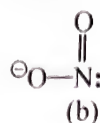
14. HNO_2 (Nitrous acid, monobasic, O.S. = +3)

HNO_2 ,

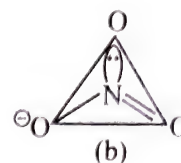
Nitrous acid (or)



NO_2^-
Nitrite ion



[One ($p\pi-p\pi$) multiple bond]



$$H = \frac{1}{2} (V + M) = (5 + 1) = 3 \quad \text{SN} = 2 \text{ bp} + 1 \text{ lp} = 3$$

$H = sp^2$, Geometry = Planar, Shape = Bent or V shape

15. Hyponitrous acid ($\text{H}_2\text{N}_2\text{O}_2$, Dibasic, O.S. = +1)

$\text{HO}-\ddot{\text{N}}=\ddot{\text{N}}-\text{OH}$

Hyponitrous acid

(a)

$\text{HO}-\ddot{\text{N}}=\ddot{\text{N}}-\text{O}^-$

Hydrogen hyponitrite ion

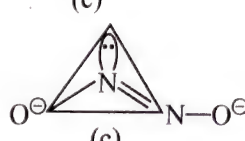
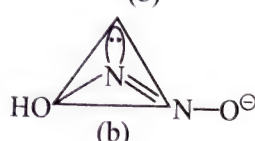
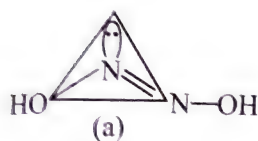
(b)

$\text{O}^- - \ddot{\text{N}}=\ddot{\text{N}} - \text{O}^-$

Hyponitrite ion

(c)

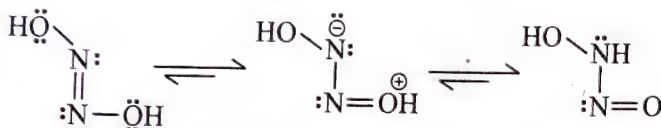
[One ($p\pi-p\pi$) multiple bond]



$$H = \frac{1}{2} (V + M) = \frac{1}{2} (5 + 1) = 3 \quad \text{SN} = 2 \text{ bp} + 1 \text{ lp} = 3$$

$H = sp^2$, G = planar Shape = Bent or shape

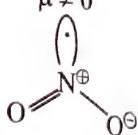
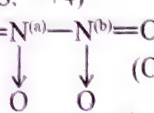
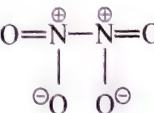
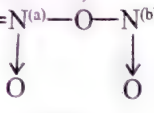
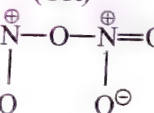
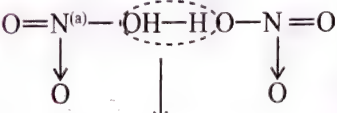
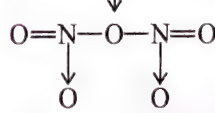
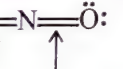

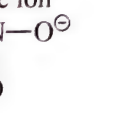
It shows tautomerism



24. Oxides of Nitrogen and their ions:

(Note: π bond is excluded in bond pair i.e., from hybridisation.)

S. No.	Oxides of nitrogen and O.S. of N	Characteristics	SN	Hyb. (H)	Geometry and shape, (G and S) and dipole moment
1.	Nitrous oxide or laughing gas (N_2O) (O.S. = +1) $\text{:N}^a \equiv \text{N}^b \rightarrow \ddot{\text{O}} \text{ :}$ or $\text{:N}^a \equiv \text{N}^b \rightarrow \text{O}^\ominus$ ↑ one bond pair	Neutral and diamagnetic 2($p\pi-p\pi$) multiple bonds	SN at $\text{N}^a = 1 \text{ bp} + 1 \text{ lp} = 2$ SN at $\text{N}^b = 2 \text{ bp} = 2$	sp	G = Linear $\mu \neq 0$
2.	Nitric oxide $\cdot\ddot{\text{N}}=\text{O}$ (O.S. = +2)	Neutral and paramagnetic ($p\pi-p\pi$) multiple bonds	SN = 1 bp + 1 lp + 1 odd electrons = 3 $H = \frac{1}{2} (V + M + \text{odd electrons})$ $= \frac{1}{2} (5 + 0 + 1) = 3$	sp^2	G = Planar Shape = Linear $\mu \neq 0$
3.	Dinitrogen trioxide (N_2O_3) (O.S. = +3) $\text{O}=\text{N}^{(a)}-\text{N}^{(b)}=\text{O}$ ↓ O or $\text{O}=\text{N}^{(a)}-\text{N}^{(b)}=\text{O}$ ↓ O^\ominus	Acidic and diamagnetic 2($p\pi-p\pi$) multiple bonds	SN at $\text{N}^a = 3 \text{ bp}$ SN at $\text{N}^b = 2 \text{ bp} + 1 \text{ lp} = 3$ $H = \frac{1}{2} (V + M)$ rule is not applicable in this case.	sp^2	G at N^a = Planar G at N^b = Planar Shape at N^b = Bent $\mu \neq 0$

4.	<p>Nitrogen dioxide (NO_2) (O.S. = +4) $\text{O} \leftarrow \text{N}=\text{O}$ (OR) $\text{O}^{\ominus}-\text{N}^{\oplus}=\text{O}$</p>	<p>Acidic and paramagnetic one ($p\pi-p\pi$) multiple bonds</p>	<p>$\text{SN} = 2\text{bp} + 1 \text{ odd electron} = 3$. $H = \frac{1}{2}(V+M) + 1 \text{ odd electron}$ $= \frac{1}{2}(5+0+1) = 3$</p>	sp^2	<p>G = Planar, Shape = Bent $\mu \neq 0$  Expected bond angle = 120° but observed bond angle = 134°</p>
5.	<p>Dinitrogen tetroxide (N_2O_4) (O.S. = +4) $\text{O}=\text{N}^{(a)}-\text{N}^{(b)}=\text{O}$  (OR) $\text{O}=\text{N}^{\oplus}-\text{N}^{\oplus}=\text{O}$ </p>	<p>Acidic and diamagnetic 2($p\pi-p\pi$) multiple bonds</p>	<p>Same SN at N^a or N^b. $\text{SN} = 3 \text{ bp} = 3$ $H = \frac{1}{2}[(V+M \pm \text{charge})]$ rule is not applicable in this case.</p>	sp^2	<p>G = Planar $\mu \neq 0$</p>
6.	<p>Dinitrogen pentaoxide (N_2O_5) (O.S. = +5) $\text{O}=\text{N}^{(a)}-\text{O}-\text{N}^{(b)}=\text{O}$  (OR) $\text{O}=\text{N}^{\oplus}-\text{O}-\text{N}^{\oplus}=\text{O}$ </p>	<p>Acidic and anhydride of HNO_3, i.e. $\text{O}=\text{N}^{(a)}-\text{OH}-\text{H}-\text{O}-\text{N}^{(b)}=\text{O}$   2 ($p\pi-p\pi$) multiple bond</p>	<p>Same SN at N^a or N^b. $\text{SN} = 3 \text{ bp} = 3$ $H = \frac{1}{2}[(V+M \pm \text{charge})]$ rule is not applicable in this case.</p>	sp^2	<p>G = Planar $\mu \neq 0$</p>
7.	<p>NO_2^{\oplus} (O.S. = +5) $:\ddot{\text{O}}=\text{N}=\ddot{\text{O}}:$  2 bond pairs (π bonds are excluded from hybridisation)</p>	<p>Acidic and diamagnetic 2 ($p\pi-p\pi$) multiple bond</p>	<p>$\text{SN} = 2 \text{ bp} = 2$ $H = \frac{1}{2}[V+M - (+\text{ve charge})]$ $= \frac{1}{2}(5+0-1) = 2$</p>	sp	<p>G = Planar Bond angle = 180° $\mu = 0$</p>
8.	<p>NO_2^{\ominus} (O.S. = +3) Nitrite ion </p>	<p>Acidic and diamagnetic one ($p\pi-p\pi$) multiple bond</p>	<p>$\text{SN} = 2 \text{ bp} + 1 \text{ lp} = 3$ $H =$ $\frac{1}{2}[V+M+\text{No. of } -\text{ve charge}]$ $= \frac{1}{2}(5+0-1) = 3$</p>	sp^2	<p>G = Planar Shape = Bent $\mu \neq 0$ Expected bond angle = 120° But observed bond angle = 115°</p>
9.	<p>NO_3^{\ominus} (O.S. = +5) Nitrite ion $\text{O}=\text{N}-\text{O}^{\ominus}$ </p>	<p>Acidic and diamagnetic 2 ($p\pi-p\pi$) multiple bond</p>	<p>$\text{SN} = 3 \text{ bp} = 3$ $H =$ $\frac{1}{2}[V+M+\text{No. of } -\text{ve charge}]$ $= \frac{1}{2}(5+0+1) = 3$</p>	sp^2	<p>G = Planar $\mu = 0$ Bond angle = 120°</p>
10.	<p>N_3^{\ominus} (Azide ion)</p>	<p>The possible linear structures are shown as: $[\text{:}\ddot{\text{N}}=\text{N}=\ddot{\text{N}}:]^{\ominus}$ (a) $[\text{:}\ddot{\text{N}}-\text{N}\equiv\text{N}:]^{\ominus}$ (b) $[\text{:}\text{N}\equiv\text{N}-\ddot{\text{N}}:]^{\ominus}$ (c) SN on the central N atom in all structures = 2 bp, $H = sp$, Geometry = linear</p>			

2.1 INTRODUCTION

Group 15 of the periodic table comprises nitrogen (N), phosphorous (P), arsenic (As), antimony (Sb) and bismuth (Bi). These elements are collectively known as **pnictogen** and their compounds as **pniconides**. The name **pnictogen** is derived from the Greek word **pnicomigs** which means suffocation. Pniconides contain E^{3-} species.

These are *p*-block elements as the last differentiating element is accommodated in *np* orbitals

2.2 OCCURRENCE

Molecular nitrogen comprises 78% (by volume) of the earth atmosphere, but it is not very abundant in the earth crust. Nitrogen is the thirty-third most abundant element by mass in the earth crust.

Nitrogen mainly occurs as nitrates i.e. chile saltpetre (NaNO_3) and Indian saltpetre (KNO_3). Nitrogen is an essential constituent of proteins and amino-acids. Nitrates and other nitrogen compounds are extensively used in fertilisers and explosives. Phosphorous is the eleventh most abundant element in the earth crust. It is highly reactive and does not occur free in nature. It occurs in minerals of the apatite family, $\text{Ca}_5(\text{PO}_4)_3\cdot\text{CaX}_2$ ($\text{X} = \text{F, Cl or OH}$) i.e. fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\cdot\text{CaF}_2$, chlorapatite, $\text{Ca}_5(\text{PO}_4)_3\cdot\text{CaCl}_2$ or hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\cdot\text{Ca}(\text{OH})_2$. These are main components of phosphate rocks. Phosphorous is an essential constituent of animal and plant matter. It is present in bones as well as in living cells. Phosphoproteins are present in milk and eggs. It also occurs in nucleic acids, i.e. DNA and RNA which control the hereditary effects in human beings and in adenosine triphosphate (ATP) and adenosine diphosphate (ADP) which are of vital importance for the production of energy in cells.

The elements As, Sb and Bi are not very abundant. Their most important source is as sulphides occurring as traces in other ores. The only common ores of arsenic are:

1. Arsenopyrites – FeAsS
2. Realgar – As_4S_4
3. Orpiment – As_2S_3

The most important ore of antimony is stibnite, Sb_2S_3 . Bismuth occurs as bismuthinite (Bi_2S_3) and bismite (Bi_2O_3).

2.3 ATOMIC AND PHYSICAL PROPERTIES

Some of the important atomic and physical properties of group 15 elements along with their electronic configurations are given in Table 2.1.

2.3.1 ELECTRONIC CONFIGURATION

The general valence shell electronic configuration of group 15 is ns^2np^3 (where $n = 2$ to 6). The three electrons in the *np* orbitals are distributed as $np_x^1 np_y^1 np_z^1$ in accordance with Hund's rule.

The *ns* orbital in group 15 elements is completely filled and *np* orbitals are half filled, making their electronic configuration extra stable.

2.3.2 ATOMIC AND IONIC RADII

1. Down the group (\downarrow), i.e. from N to Bi, the covalent (atomic) and ionic radii (in a particular oxidation state) increases. There is considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed.

Explanation: Down the group (\downarrow), i.e. from N to Bi, with addition of a new principal energy shell in each succeeding element, effective nuclear charge decreases and covalent radii increases. But the increase in radii at each step is not the same due to difference in electronic configuration of N and P on one hand and As, Sb and Bi on other hand. In N and P, the valence shell electrons are preceded by noble gas core, hence shielding effect is very high and thus decrease in effective nuclear charge is high and there is considerable increase in radii from N to P. But in As, Sb and Bi, in between the valence shell electrons and noble gas core lesser shielding fully filled *d* and/or *f* orbitals are present. Thus shielding effect is less and effective nuclear charge increases which reduces the effect of addition of a new energy shell to some extent. Hence from As to Bi, increase in covalent radii is very less.

Table 2.1 Atomic and physical properties of Group 15 element

Elements	Nitrogen	Phosphorous	Arsenic	Antimony	Bismuth
Symbol	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Atomic mass/(g mol ⁻¹)	14.01	30.97	74.92	121.75	208.98
Electronic configuration	[He] $2s^2 2p^3$	[Ne] $3s^2 3p^3$	[Ar] $3d^{10} 4s^2 4p^3$	[Kr] $4d^{10} 5s^2 5p^3$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^3$
Ionisation enthalpy/(kJ mol ⁻¹)	I	1402	947	834	703
	II	2856	1798	1595	1610
	III	4577	2736	2443	2466
Electronegativity	3.0	2.1	2.0	1.9	1.9
Covalent radius/(pm) ^a	70	110	121	141	148
Ionic radius/(pm)	171 ^b	212 ^b	222 ^b	76 ^c	103 ^c
Melting point / (K)	63 ^d	317 ^c	1089 ^f	904	544
Boiling point/(K)	772 ^d	554 ^c	888 ^g	1860	1837
Density at 298 K/(g cm ⁻³)	0.879 ^h	1.823	5.778 ⁱ	6.697	9.808

^a E^{III} single bond ($E = \text{element}$); ^b E^{3-} ; ^c E^{3+} ; ^dMolecular nitrogen; ^ewhite phosphorous; ^fGrey (α -form) at 38.6 atm; ^gsublimation temperature; ^hat 63 K; ⁱGrey α -form.

2. The atomic radii of elements of group 15 are less than the corresponding elements of group 14.

Explanation: From left to right (\rightarrow) i.e. from group 14 to 15 in a given period, with increase in nuclear charge, the electron is added in the same shell. Consequently, the effective nuclear charge increases and covalent radii decreases.

e.g. atomic or covalent radii of N is less than carbon.

2.3.3 IONISATION ENTHALPY (IE OR ΔH^\ominus)

The ionisation enthalpies of the elements of group 15 are much higher than the corresponding elements of group 14. Down the group (\downarrow) the values of the ionisation energies decrease.

Explanation: Because of increased nuclear charge, reduced atomic radii and stable half-filled configurations, they have much less tendency to lose electrons as they are more tightly held by the nucleus. Consequently the ionisation enthalpies of group 15 elements are much higher as compared to elements of group 14 carbon family. The decrease in their values, down the group is due to gradual increase in the atomic size which reduces the force of attraction on the electrons by the nucleus.

IE: $N > P > As > Sb > Bi$

2.3.4 ELECTRONEGATIVITY (EN)

Group 15 elements are more electronegative than group 14 elements. Electronegativity of elements of group 15 shows a gradual decrease down the group from N to Bi.

Explanation: As the elements of group 15 have smaller atomic size and need less number of electrons to attain noble gas configuration as compared to elements of group 14, they are more electronegative. Down the group, due to the gradual increase in the atomic size, attraction by the nucleus for the electrons decreases. Hence their electronegativity values decrease down the group.

EN: $N > P > As > Sb > Bi$

2.3.5 MELTING AND BOILING POINTS

The melting points of group 15 elements first increase from nitrogen to arsenic and then decrease to antimony and bismuth. The melting points of antimony and bismuth are less than the expected values. The boiling points, however, increase regularly from N to Bi.

Explanation: The melting points increase down the group due to increase in their atomic size. The unexpected decrease in the melting points of antimony and bismuth is because of their tendency to form three covalent bonds instead of five covalent bonds due to **inert pair effect**. This results in weakening the attraction among their atoms thus lowering their melting points. Because of larger size of atoms, bismuth has still weaker interatomic forces than antimony and thus has lower melting points.

Melting points: $N < P < Bi < Sb < As$

Down the group (\downarrow), i.e. from N to Bi, boiling points increase due to an increase in their atomic size (exception $P < N$).

Boiling points: $P < N < As < Bi < Sb$

2.3.6 DENSITY

The density of the element of group 15 increases regularly from N to Bi as usual.

2.3.7 METALLIC CHARACTER

Metallic character increases down the group (\downarrow) from N to Bi.

Explanation: Down the group, the atomic size increases and the outer electrons get farther from the nucleus. The ionisation energy decreases and the electrons become more loosely held and have a tendency to be lost readily. Thus the metallic character increases. First two elements of this group (N and P) are non-metals, the next two (As and Sb) are metalloids, while Bi is a typical metal. Thus the metallic character increases from N to Bi.



The elements of group 15 are less metallic than the corresponding elements of group 14. This is due to increase in nuclear charge and electronegativity from group 14 to group 15, hence the metallic character decreases from group 14 to 15.

2.3.8 ATOMIC AND PHYSICAL STATE

Nitrogen exists as diatomic gaseous molecule, phosphorous, arsenic and antimony exist as discrete tetrahedra tetraatomic solid molecules and bismuth is metallic at ordinary temperature.

2.3.9 $p\pi-p\pi$ MULTIPLE BOND

Nitrogen because of its small size and high electronegativity forms $p\pi-p\pi$ **multiple** bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Thus, nitrogen exists as a diatomic molecule with a triple bond ($N \equiv N$, one σ - and two π - bonds) between the two atoms. These N_2 molecules are held together by weak **van der Waals** forces of attraction which can be easily broken by the collisions of the molecules at room temperature. Therefore, N_2 is a gas at room temperature. Since bond dissociation enthalpy ($941.4 \text{ kJ mol}^{-1}$) of $N \equiv N$ molecule is very high, N_2 is an inert gas.

The other elements of group 15 do not form $p\pi-p\pi$ **multiple** bonds since their atomic orbitals are large and diffused that they cannot have effective overlapping. Thus, P, As and Sb do not form $p\pi-p\pi$ **multiple** bonds. Instead they prefer to form single bonds as $P-P$, $As-As$ and $Sb-Sb$ while Bi forms metallic bonds in the elemental state. Actually, phosphorus, arsenic and antimony exist as discrete tetraatomic tetrahedral molecules such as P_4 , As_4 , Sb_4 , etc. containing E—E single bonds.

Due to bigger size, the forces of attraction holding the tetraatomic molecules of P_4 , As_4 , Sb_4 , etc. are quite strong and hence cannot be broken by the collisions of the molecules at room temperature. Therefore, P_4 , As_4 , Sb_4 all are solids at room temperature.

2.3.10 CATENATION

The elements of group 15 also show the property of catenation (self-linking of atoms) but to a much smaller extent than elements of group 14. The reason being that the E—E bond strength of these elements is much lower than that of C—C bond.

Bond	C—C	N—N	P—P	As—As
Bond strength (kJ mol^{-1})	347	159	213	1474

Among the elements of group 15, phosphorus has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorus atoms.

Nitrogen has little tendency for catenation since N—N single bond is very weak due to large interelectronic repulsions between the lone pairs of electrons present on the N-atoms of N—N bond having small bond length. As a result the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of *d* orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form $d\pi-d\pi$ bond as the heavier elements can e.g., $R_3P=O$ or $R_3P=CH_2$ (*R* = alkyl group). Phosphorus and arsenic can form $d\pi-d\pi$ bond also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

Nitrogen can form chains containing up to three N-atoms, e.g., hydrazoic acid, N_3H or azide ion, N_3^- ion. Due to decrease in E—E bond strength down the group, catenating ability decreases from P to As. As can form a chain of only two atoms.

2.4 CHEMICAL PROPERTIES

2.4.1 OXIDATION STATES

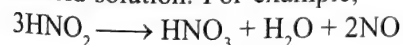
The elements of group 15 have $ns^2 np^3$ as their valence shell electronic configuration. They can complete their octets in two different ways:

- 1. Electron transfer:** The atoms of the elements of this group may accept three electrons from more metallic elements to form triply charged negative ions such as nitride, N^{3-} ion and phosphide, P^{3-} ion and thereby attain noble gas configuration. Only small atoms can form highly charged negative ions because of their greater electronegativities. Obviously nitrogen with greater electronegativity and smaller size, has a stronger tendency to form triply charged negative ions and this tendency decreases down the group because of increase of size and decrease in electronegativity.

The elements of this group also exhibit +3 and +5 oxidation states. The +5 ions are generally not known because their sizes will be very small and their ionisation energy will be very high. Down the group, the stability of +3 oxidation state increases while that of +5 decreases. This is due to **inert pair effect** as ns^2 electrons tend to remain paired in heavier *p*-block elements i.e., they do not take part in the bond formation. It is due to the fact that *s*-electrons are penetrating in the preceding shell in such a way that they are a part of inner shell electrons and are, therefore, removed with difficulty.

Bi^{3+} and Sn^{3+} are stable due to decrease in IE. BiF_3 is known, but BiF_5 is not.

Besides -3, N and P also show oxidation states of -2 in hydrazine (NH_2NH_2) and diphosphine (PH_2PH_2) respectively. Nitrogen also shows an oxidation state -1 in hydroxylamine (NH_2OH) but phosphorous does not. In case of nitrogen, all O.S. from +1 to +4 bend to disproportionate in acid solution. For example,



- 2. Electron sharing:** Since the atoms of these elements contain three unpaired *p*-electrons so these can pair with unpaired electrons in another atom or atoms to form covalent bonds e.g., NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3 .

2.4.2 MAXIMUM COVALENCY

Since nitrogen does not possess any vacant *d*-orbitals in its valence shell ($n = 2$), it, therefore, cannot extend its valency beyond four [NH_4^+ , NR_4^+]. That is the reason why nitrogen does not form NF_5 or NCl_5 . On the other hand, phosphorous and other elements have empty *d*-orbitals and can utilise all their valence electrons to exhibit covalency of five or six, e.g. PCl_5 , $[SbF_6]^-$, AsF_5 , $[PF_6]^-$.

2.4.3 NATURE OF BONDING

In majority of the compounds of these elements the bonds are covalent. Nitrogen and phosphorous are predominantly covalent though they may form ionic nitrides and phosphides by accepting 3 electrons. The strength of the covalent bonding decreases down the group (\downarrow) i.e. covalent bonding strength is in the order:



2.5 CHEMICAL REACTIVITY

2.5.1 REACTIVITY TOWARDS HYDROGEN —FORMATION OF HYDRIDE

All the elements of group 15 form volatile hydrides having formula EH_3 , where E = N, P, As, Sb and Bi.

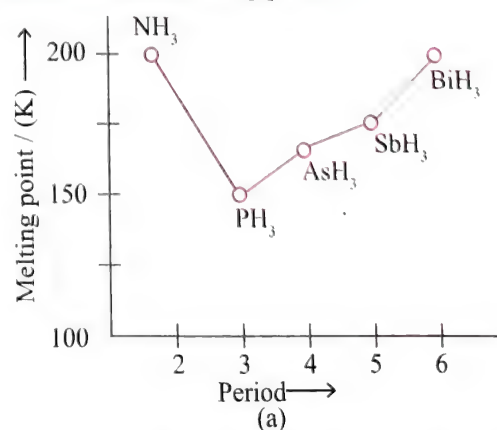
Bond angle: According to VSEPR theory, lone pair—bond pair (lp—bp) repulsion is greater than bond pair—bond pair (bp—bp) repulsion, this leads to contraction in the bond angle, i.e. bond angle is less than 109.28° (Tetrahedral angle). Consequently, all the group 15 hydrides have pyramidal shape. The bond angles are as follows:

NH_3	PH_3	AsH_3	SbH_3	BiH_3
107.8°	93.6°	91.8°	91.3°	90°

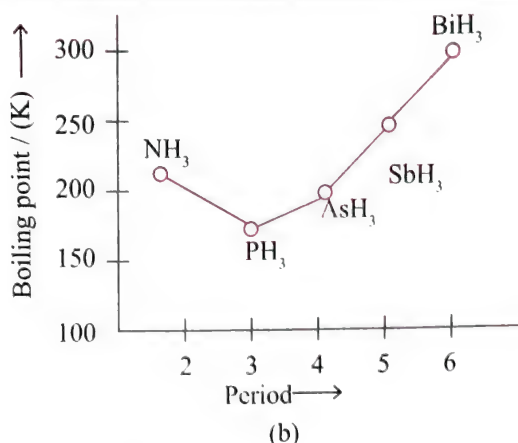
Explanation: The decrease in the bond angle can be explained on the basis of the size and electronegativity of the central atom. Due to small size and high electronegativity of N-atom, the electron density on N-atom is highest. So repulsions between the electron pairs is maximum and so is the bond angle. From N to Bi, size increases and electronegativity decreases. This results in decrease of electron density on the central atom. As a result, the repulsion between the electron pairs decreases and hence the bond angle also decreases.

2.5.2 CHARACTERISTICS OF HYDRIDES

1. Melting point and boiling point :



[Melting point: NH_3 (195.2) > BiH_3 (≈ 190) > SbH_3 (185) > AsH_3 (156.7) > PH_3 (139.5) K]



[Boiling point: BiH₃ (290) > SbH₃ (254.6) > NH₃ (238.5) > AsH₃ (210.6) > PH₃ (185.5) K]

Fig. 2.1 (a) and (b) Melting and boiling points of hydrides of group 15

Explanation of hydrides of group 15

Melting point

The melting point of NH₃ is highest in the hydrides of group 15 due to intermolecular H-bonding.

In this case increased molecular masses of BiH₃ and SbH₃ do not affect so much the melting point of NH₃. Because the increased **van der Waals** forces are not so strong in the solid state as they are in liquid state.

OR

The H-bonding in NH₃ is stronger in the solid state than in the liquid or gaseous state.

Boiling point

The boiling point of NH₃ is slightly lower than those of BiH₃ and SbH₃ due to their high molecular mass as compared to that of NH₃. The increased molecular masses of BiH₃ and SbH₃ increases the **van der Waals** forces of attraction in liquid state.

OR

The H-bonding in NH₃ is weaker in the liquid or gaseous state than in solid state.

Reducing agent: NH₃ > PH₃ > AsH₃ > SbH₃ > BiH₃

4. **Basic character:** Ammonia is the strongest base among them. Down the group, the basic character of the hydrides of the elements of group 15 decreases. PH₃ is a much weaker base than NH₃, AsH₃, SbH₃ and BiH₃ are not basic at all.

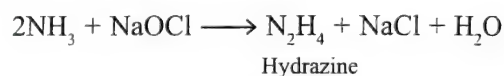
Explanation: The basic character of the hydrides of group 15 is due to the lone pair of electrons on the central atom in them (called Lewis bases).

Since the size of nitrogen atom is small, the lone pair of electrons is distributed over a small volume. As a result electron density on N is high and hence ammonia is strongly basic. Down the group, the size of the atoms (P, As, Bi etc.) goes on increasing and the lone pair of electrons is distributed over a large volume. As a result electron density decreases and, therefore, the basic strength of their respective hydrides keeps on decreasing.

5. **Solubility:** Because of tendency towards hydrogen bonding with water molecules, ammonia is soluble in water while PH₃ and other hydrides are insoluble in water.

Nitrogen and phosphorus form two other important hydrides, i.e. hydrazine (N₂H₄) and diphosphine (P₂H₄)

Hydrazine: It is prepared by the oxidation of ammonia with NaOCl (sodium hypochlorite)



Hydrazine is a strong reducing agent. Hydrazine and its derivatives are used as rocket fuels.

2.5.3 REACTIVITY TOWARDS OXYGEN (OXIDE FORMATION)

Nitrogen due to its small size has a strong tendency to form $p\pi-p\pi$ multiple bonds between N and O atoms, while other elements of group do not. Hence nitrogen forms a number of oxides which have no P, As, Sb or Bi analogues. For example, N₂O is known but P₂O is not known.

2.5.4 PROPERTIES OF OXIDES

- Oxides of non-metals are acidic, those of metalloids are amphoteric while those of metals are basic.
- Greater the electronegativity of the element, more acidic is the oxide.
- Among the oxides of the same element, higher the oxidation state of the element, more is its acidic strength.

The oxides of the type E₂O₃ of N and P are purely acidic that of As, and Sb amphoteric and those of Bi are predominantly basic.

(1) Acidic strength of oxides of nitrogen increases in the order: N₂O < NO < N₂O₃ < N₂O₄ < N₂O₅ < N₂O and NO are, however, neutral.

b. Acidic strength of trioxides follows the order.

2. **Thermal stability:** The thermal stability of hydrides of the elements of group 15 decreases gradually from NH₃ to BiH₃. SbH₃ and BiH₃ are thermally unstable whereas BiH₃ has been obtained in traces only.

Down the group (↓) as the bond length (internuclear) distance between hydrogen and group 15 element increases, the bond strength E-H decreases and consequently thermal stability decreases.

Thermal stability: NH₃ > PH₃ > AsH₃ > SbH₃ ≥ BiH₃

3. **Reducing agent:** The reducing character of hydrides of group 15 elements increases down the group. Because of decrease in thermal stability from NH₃ to BiH₃. The tendency to give hydrogen and act as reducing agent gradually increases from NH₃ to BiH₃. The reducing character thus depends on the instability of the hydride. The greater the instability, greater is its reducing property. Except NH₃, all the hydrides are strong reducing agents. They react with metal ions (Ag⁺, Cu²⁺ to form their phosphides, arsenides and antimonides respectively.



In fact, As_4O_6 and Sb_4O_6 are amphoteric while Bi_2O_3 is basic in nature.

c. Acidic strength of pentoxides follows the order:

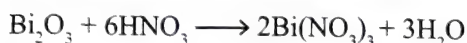


d. Due to their large size, P, As, Sb and Bi are reluctant to form $p\pi-p\pi$ multiple bond and their oxides as tetramers, X_4O_6 , X_4O_8 and X_4O_{10} . Preparation and properties of oxides of phosphorous are given in the following table and their structures are given below.

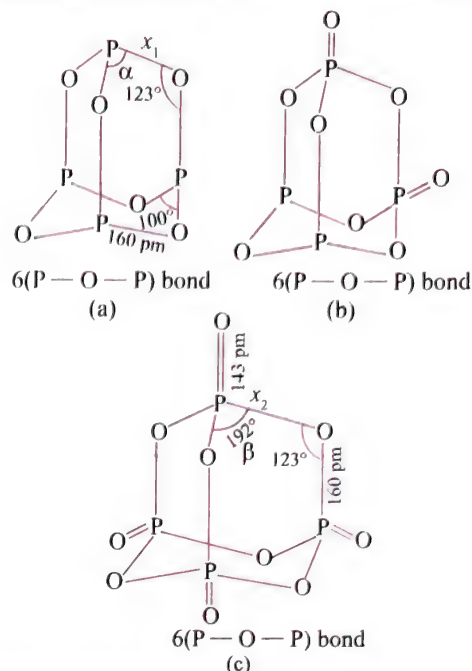
e. Trioxide of As and Sb are prepared by heating the elements in limited supply of oxygen.



Bi_2O_3 dissolves in acids to give salts



Among group 15 elements, Bi alone forms a stable nitrate, sulphate or carbonate and thus behaves like a metal. Structures of P_4O_6 , P_4O_8 and P_4O_{10} are given in Fig. 2.2.



Note : According to Bent's rule $x_1 > x_2$ and $\alpha < \beta$.

Fig. 2.2 Structure of (a) Phosphorous trioxide (P_4O_6), (b) Phosphorous tetroxide (P_4O_8) and (c) Phosphorous pentoxide (P_4O_{10})

Table 2.2 Preparation and properties of oxides of phosphorous

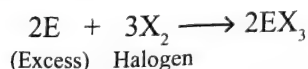
Oxides	Oxidation	Preparation	Oxides of arsenic
Phosphorous, P_4O_6	+3	Burning white P_4 in limited supply of air $\text{P}_4 + 3\text{O}_2 \rightarrow \text{P}_4\text{O}_6$	<ul style="list-style-type: none"> White waxy solid, garlic smell Soluble in ether, benzene, CS_2, CHCl_3 With cold water phosphorous acid is formed $\text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_3$ With hot water, $\text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 3\text{H}_3\text{PO}_4 + \text{PH}_3$
Phosphorous tetraoxides, P_4O_8	+4	Heating P_4O_6 at 210°C in absence of air $4\text{P}_4\text{O}_6 \xrightarrow{210^\circ\text{C}} 3\text{P}_4\text{O}_8 + \text{P}_4 \text{ (Red)}$	On hydrolysis gives phosphorous acid and phosphoric acid $\text{P}_4\text{O}_8 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_3 + 2\text{H}_3\text{PO}_4$
Phosphorous pentoxide, P_4O_{10}	+5	Heating white P_4 in excess of air $\text{P}_4 + 5\text{O}_2 \rightarrow \text{P}_4\text{O}_{10}$	<ul style="list-style-type: none"> $\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4$ Phosphoric acid Acts as an excellent dehydrating agent $2\text{HClO}_4 + \text{P}_4\text{O}_{10} \rightarrow \text{Cl}_2\text{O}_7 + \text{P}_4\text{O}_{10} \cdot \text{H}_2\text{O}$

2.5.5 REACTIVITY TOWARDS HALOGENS (HALIDE FORMATION)

Group 15 elements react to form two series of halides: EX_3 and EX_5 .

2.5.5.1 Trihalides, EX_3

1. **Preparation:** The elements directly combine with halogen to form trihalides, when the group 15 element is in excess.



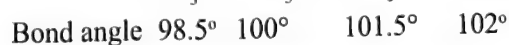
2. **Structures:** All the trihalides have pyramidal structure.

In all the trihalides, the central halogen atom is sp^3 hybridised with 1 lp

Three of the four sp^3 hybrid orbitals overlap with np orbital of the halogen atom to form σ bond. The fourth sp^3 orbital

contains lone pair of electrons. According to VSEPR theory, since the lone pair–bond pair (lp–bp) repulsion is greater than bond pair–bond pair (bp–bp) repulsion, contraction in the bond angle occurs, hence bond angle in all the trihalides is less than 109.4° and they have pyramidal shape.

The bond angle of the trihalides of an element increases with the decrease in electronegativity of the halogen atom and increase in the size of the halogen atom.



With the decrease in the electronegativity of the halogen atom, bond pairs remain more close to the central atom and hence bp–bp repulsion increases and bond angle increases.

3. Properties:

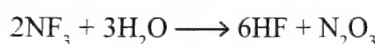
a. All the trihalides are predominantly covalent with the ionic character increasing down the group. Thus, BiF_3 is predominantly ionic while other halides of Bi, i.e. BiCl_3 , BiBr_3 , etc. and SbF_3 are partly covalent and partly ionic.

b. Of all the trihalides, trihalides of N, i.e. NCl_3 , NBr_3 and NI_3 are least stable. However, NF_3 is stable. NCl_3 is explosive, while NBr_3 and NI_3 are known only as their unstable ammoniates i.e. $\text{NBr}_3 \cdot \text{NH}_3$ and $\text{NH}_3 \cdot \text{NI}_3$. $\text{NI}_3 \cdot \text{NH}_3$ is stable only in moist state. In dry state it explodes with noise when struck liberating vapours of I_2 . Thus it is a mild and harmless explosive.

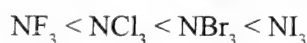


The instability of NCl_3 , NBr_3 and NI_3 is due to weakness of N-X bond due to large difference in size of N and X atoms. In NF_3 , as the difference in size of N (75 pm) and F (172 pm) is small N-F bond is quite strong. Consequently, NF_3 does not undergo hydrolysis with water, dilute acids or alkalis.

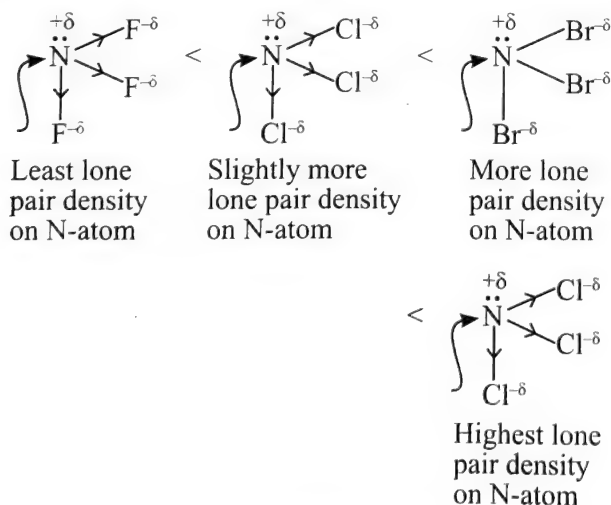
c. **Lewis base strength of NX_3 :** Due to the presence of lone pair of electrons on N-atom and absence of d -orbitals, N-atom donates its lone pair of electrons and thus behave as Lewis bases. NF_3 behaves differently from the others. It is unreactive like CF_4 and does not hydrolyse with H_2O , dilute acids or alkalis, but reacts if sparkled with water vapour.



Lewis base strength decreases from NF_3 to NI_3 , i.e.

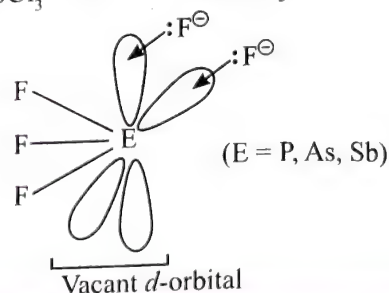
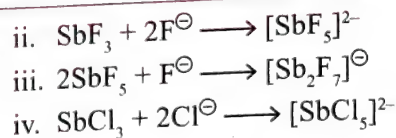
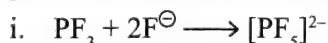


With the increase in electronegativity of halogen atom, the bond pair of N-X shifts more and more towards X-atom, hence availability of lone pair on N-atom for donation decreases and Lewis base strength decreases from NF_3 to NI_3 (EN order: $\text{F} > \text{Cl} > \text{Br} > \text{I}$).



d. Lewis acid strength of trihalides of P, As and Sb:

The trihalides of P, As, Sb (especially the fluorides and chlorides) due to the presence of d -orbitals, accept lone pair of electrons and thus behaves as Lewis acids, e.g.,

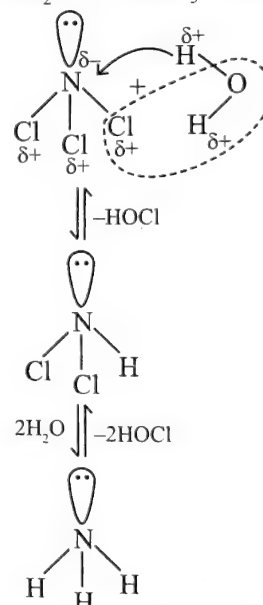
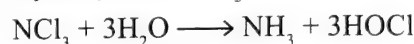


Note: PF_3 can act as donor molecules using their lone pair to form a coordinate bond. It is very similar to CO as a ligand. PF_3 is less reactive towards water and is more easily handled than other halides.

e. **Hydrolysis:** Trihalides readily undergo hydrolysis but the product of hydrolysis depends on the nature of the bond and on the element.

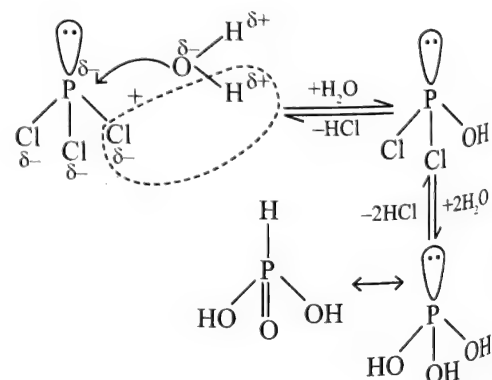
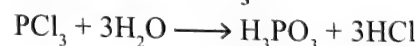
i. NF_3 does not undergo hydrolysis, due to high N-F bond strength.

ii. Hydrolysis of NCl_3 :



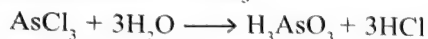
In NCl_3 , N is more electronegative than Cl, hence N interacts with the positive part of H_2O molecule and NH_3 molecule is formed, resulting in the elimination of hypochlorous acid (HOCl)

iii. Hydrolysis of PCl_3 :



On the other hand in PCl_3 , P is less electronegative than Cl and P has vacant d -orbital, hence P interacts with negative part of H_2O molecule resulting in the formation of P—OH bond and elimination of HCl molecule. Consequently H_3PO_3 is formed on hydrolysis of PCl_3 .

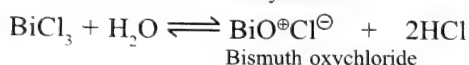
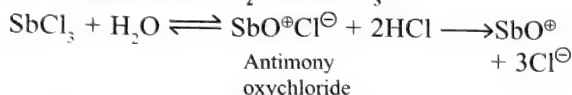
iv. Hydrolysis of AsCl_3 :



Trichlorides of As on hydrolysis gives arsenic acid (H_3AsO_3) and HCl.

Trichlorides of Bi and Sb are only partly and reversibly hydrolysed to give HCl and oxychloride of the corresponding metal, i.e.

v. Hydrolysis of SbCl_3 and SnCl_3 :



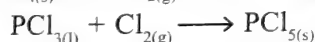
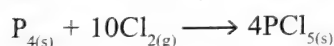
According to **Le Chatelier principle**, the addition of excess of HCl suppresses the hydrolysis by shifting the equilibrium to the left.

2.5.5.2 Pentahalides, EX_5

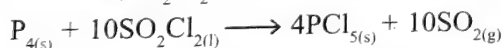
1. Nitrogen does not form pentahalides, NX_5 as N due to absence of d -orbitals in its valence shell cannot expand its coordination number beyond 4.

Phosphorous pentachloride, PCl_5 :

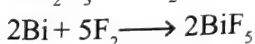
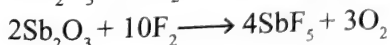
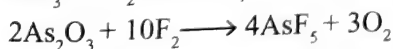
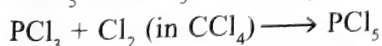
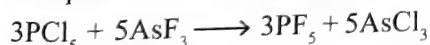
- (1) Phosphorous pentachloride is prepared by the reaction of white phosphorous with excess of dry chlorine or by the action of dry chlorine on phosphorous trichloride.



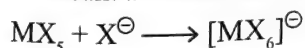
- It can also be prepared by the action of sulphuryl chloride (SO_2Cl_2) on white phosphorous.



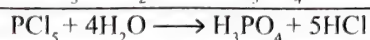
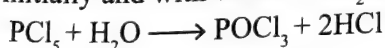
- AsCl_5 is highly reactive and unstable and has only a temporary existence. BiF_5 is highly reactive, and explodes with water, forming O_3 and F_2O . It oxidises UF_4 to UF_6 and BrF_3 to BrF_5 , and fluorinates hydrocarbons. The pentahalides are prepared as follows:



2. All the pentahalides behave as **Lewis acids** due to presence of vacant d -orbital on the central atom.



3. PF_5 does not undergo hydrolysis due to high stability of P—F bond as compared to P—O bond. However, all other pentahalides of P, undergo hydrolysis to give POCl_3 initially and with excess of H_2O gives H_3PO_4 .



4. Pentahalides are thermally less stable than the corresponding trihalides, e.g. thermal stability of PCl_5 is less than PCl_3 .

$$\text{PCl}_5 \xrightarrow{\Delta} \text{PCl}_3 + \text{Cl}_2$$

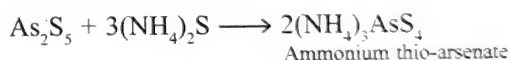
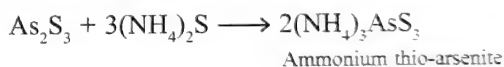
That is why PCl_5 behaves as a good chlorinating agent.

5. **Structure:** In gaseous state, PX_5 are covalent and have trigonal bipyramidal structure as P is sp^3d hybridised. Whereas in solid state, pentahalides of phosphorous are ionic and exist as given below.

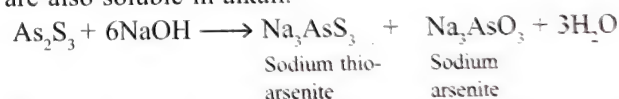
PX_5	Gas	Solid
Phosphorous pentachloride	PCl_5	$[\text{PCl}_4]^+ [\text{PCl}_6]^-$
Phosphorous pentabromide	PBr_5	$[\text{PBr}_4]^+ [\text{Br}]^-$
Phosphorous penta iodide	PI_5	$[\text{PI}_4]^+ [\text{I}]^-$

2.5.6 REACTIVITY TOWARDS METALS

1. All the group 15 elements react with metals to form their binary compounds exhibiting -3 oxidation state, such as Ca_3N_2 (calcium nitride), Ca_3P_2 (calcium phosphide) Na_3As_2 (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).
2. **Sulphide formation:** Except nitrogen all other group 15 elements form sulphides. The sulphides of arsenic and antimony are soluble in yellow ammonium sulphide or ammonium sulphide and form thio-compounds.



Antimony sulphides form similar compounds. The sulphides are also soluble in alkali.



The stability of sulphides increases with increase in atomic number of the element.

2.6 ANOMALOUS BEHAVIOUR OF NITROGEN

Nitrogen shows anomalous behaviour and differs from rest of the members of its family due to:

- i. Small size
- ii. High electronegativity
- iii. High ionisation enthalpy
- iv. Non-availability of d -orbitals in its valence shell.

Some important properties in which nitrogen differs from other members of group 15 are as follows:

1. Nitrogen exists as a diatomic (N_2) gas, while others exist as tetrahedral tetraatomic solid molecules (P_4 , As_4 and Sb_4).
2. Nitrogen shows less catenating ability than phosphorous.

3. Nitrogen is inert and unreactive in its elemental state, whereas others are highly reactive.
4. Nitrogen due to absence of d -orbitals in its valence shell shows a maximum covalency of four, i.e. nitrogen cannot expand its covalency beyond four, e.g. NH_4^+ . Other group 15 elements due to presence of vacant d -orbitals in their valence shell can have a coordination number 5 or 6 e.g. PF_5 , $[\text{PF}_6]^-$.
5. Nitrogen due to absence of d -orbitals in its valence shell, cannot form $d\pi-p\pi$ bonds, whereas others can. For example, $\text{R}_3\text{N}=\text{O}$ does not exist, but $\text{R}_3\text{P}=\text{O}$ exists.
6. Due to small size and high electronegativity, nitrogen forms trinegative N^{3-} ion. This tendency is less in phosphorous and absent in others.
7. Hydride of nitrogen, NH_3 is stable, while other hydrides are not stable. NH_3 is capable of forming hydrogen bonding while others do not.
8. Nitrogen forms five oxides (N_2O , NO , N_2O_3 , NO_2 or N_2O_4 and N_2O_5). Whereas, phosphorous forms three dimeric oxides (P_4O_6 , P_4O_8 , P_4O_{10}). Arsenic and antimony form only two dimeric oxides (As_4O_6 , As_4O_{10} , Sb_4O_6 , Sb_4O_{10}). Bismuth forms Bi_2O_3 only.
9. Except NF_3 , the other trihalides of nitrogen, i.e. NCl_3 , NBr_3 and NI_3 are unstable. On the other hand, trihalides of other elements stable.
10. Nitrogen does not form pentahalides, whereas P, As and Sb form pentahalides.
11. Nitrogen shows a large number of oxidation states from -3 to $+5$ other group 15 elements show a limited number of oxidation states.

ILLUSTRATION 2.1

- a. Though nitrogen exhibits $+5$ oxidation state, it does not form pentahalide. Give reason.
- b. PH_3 has lower boiling point than NH_3 . Why?

- Sol.**
- a. Electronic configuration of nitrogen is $1s^2 2s^2 2p^3$. Due to absence of d -orbitals in its valence shell, nitrogen cannot expand its coordination number beyond four. That is why nitrogen does not form pentahalides.
 - b. Nitrogen is more electronegative than phosphorous and hence capable of forming hydrogen bonds. Due to association of NH_3 molecules by hydrogen bonding, ammonia has higher boiling point. On the other hand, due to absence of hydrogen bonding in PH_3 molecules are not associated and PH_3 has lower boiling point than NH_3 .

ILLUSTRATION 2.2

- a. PF_5 is known, but NF_5 is not. Why?
- b. The experimentally determined $\text{N}-\text{F}$ bond length in NF_3 is greater than the sum of single covalent radii of N and F.

- Sol.**
- a. Phosphorous has vacant d -orbital in its valence, hence P can have covalency of five and PF_5 exists. But, N due to absence of d -orbital in its valence shell cannot have covalency of five, hence NF_5 is not known.
 - b. Due to their smaller size and high electron density, experimentally determined $\text{N}-\text{F}$ bond length is high, because of repulsion of bonded pair of both N and F atoms.

ILLUSTRATION 2.3

- a. Why elemental phosphorous does not exist as P_2 like N_2 ?
- b. NCl_3 gets easily hydrolysed, while NF_3 does not. Why?

- Sol.**
- a. Nitrogen due to its small size has a tendency to form multiple bond and thus exists as diatomic molecule. Phosphorous, on the other hand, has comparatively large size, therefore, extent of overlap of $(3p-3p)$ which can result in π -bond formation is less, and phosphorous has no tendency to form multiple bond with itself. Hence phosphorous does not exist as P_2 molecule.
 - b. In NCl_3 , N is more electronegative than Cl, hence N has δ^- charge and Cl has δ^+ charge, moreover due to presence of vacant d -orbital on Cl, it accepts a pair of electron from O atom of H_2O molecule. Thus hydrolysis is possible. On the other hand, in NF_3 due to high $\text{N}-\text{F}$ bond strength, NF_3 molecule is inert and does not undergo hydrolysis.

ILLUSTRATION 2.4

- a. Can PCl_5 act as an oxidising as well as reducing agent?
- b. Phosphorous does not form phosphorous pentaiodide. Why?

- Sol.**
- a. In PCl_5 , oxidation state of P is $+5$. Phosphorous can exhibit a maximum oxidation state of $+5$. Since P cannot have oxidation state greater than $+5$. Therefore, it cannot get oxidised and thus PCl_5 cannot act as reducing agent. However, P can have lower oxidation state as compared to $+5$, and thus can get reduced and PCl_5 behave as oxidising agent.
 - b. Due to large size of iodine, phosphorous cannot accommodate five iodine atoms around it, and hence PI_5 does not exist. Moreover EN of iodine is too low to excite $3s^2$ electron to $3d$ orbitals for the formation of five bonds.

ILLUSTRATION 2.5

- a. Heavier metals of 15 group do not form $p_\pi-p_\pi$ bonds. Why?
- b. Why $\text{N}-\text{N}$ bond is weaker than single $\text{P}-\text{P}$ bond.

- Sol.**
- a. Nitrogen has unique ability to form $p_\pi-p_\pi$ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Heavier metals of this group do not form $p_\pi-p_\pi$ bonds.

as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, Nitrogen exists as diatomic molecule with a triple bond (one *s* and two *p*) between two atoms.

Consequently, its bond enthalpy ($971.4 \text{ kJ mol}^{-1}$) is very high. On the contrary, P, As and Sb form single bonds as P—P, As—As and Sb—Sb while Bi forms metallic bond in elemental state.

- b. It is due to high interelectronic repulsion of the non-bonding e^{-} s, owing to the small bond length. As a result catenation tendency is weaker in nitrogen.

2.7 DINITROGEN (N_2)

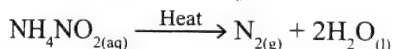
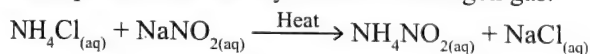
Nitrogen exists as a diatomic gas, N_2 in the elemental state, hence it is also known as dinitrogen.

Preparation:

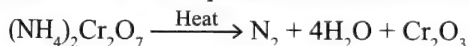
- Commercial method:** Dinitrogen is prepared commercially by the liquefaction and fractional distillation of air. On distillation, liquid dinitrogen having lower boiling point (77.2 K) distills out first leaving behind liquid oxygen having higher boiling point (90 K).

- Laboratory method:**

- By heating an equimolar aqueous solution of ammonium chloride (NH_4Cl) with sodium nitrite, (NaNO_2). As a result of double decomposition reaction, ammonium nitrite (NH_4NO_2) is formed first, which being unstable decomposes immediately to form dinitrogen gas.



- By thermal decomposition of ammonium dichromate:



Ammonium dichromate (orange)	Chromic oxide green
------------------------------------	---------------------------

- By thermal decomposition of sodium or barium azide:

Very pure nitrogen can be obtained by this method.



Thermal decomposition of sodium azide is used to inflate the air bags used for safety devices in cars.

2.7.1 PROPERTIES

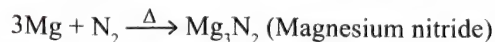
2.7.1.1 Physical Properties

- Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.
- Nitrogen atom has two stable isotopes: ^{14}N and ^{15}N .
- It has very low solubility in water (23.2 mL/L of water at 273 K and 1 bar pressure).
- It has low freezing (63.2 K) and boiling point (77.2 K).
- It is absorbed by activated charcoal.

2.7.1.2 Chemical Properties

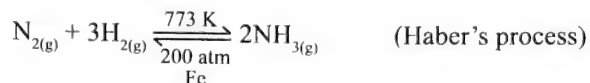
- Dinitrogen is an inert gas due to very small $\text{N}\equiv\text{N}$ bond length and hence high bond dissociation enthalpy. However, reactivity increases with increase in temperature.

- Reaction with metal:** The nitrides formed with active metals are predominantly ionic.

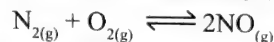


- Reaction with non-metals:** Dinitrogen reacts with non-metals to form predominantly covalent nitrides.

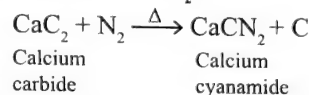
- With H_2 , N_2 reacts at $\sim 773 \text{ K}$ and 200 atm in the presence of Fe as catalyst to form ammonia.



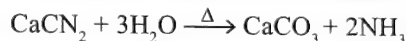
- With O_2 , N_2 combines at a very high temperature, i.e. $\sim 2000 \text{ K}$ form nitric oxide, NO .



- Reaction with CaC_2 :**



- Calcium cyanamide reacts with water to form NH_3 , hence, it is used as a fertiliser under the name Nitrolim ($\text{CaCN}_2 + \text{C}$).

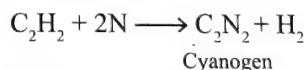


Uses:

- In the manufacture of ammonia and other industrial chemical containing nitrogen, e.g. calcium cyanamide.
- To provide an inert atmosphere in iron and steel industry. It also acts as a inert diluent (for reactive chemicals).
- Liquid nitrogen is used as a refrigerant, to preserve biological materials, food items and in cryosurgery.
- In gas filled thermometers, which are used for measuring high temperatures.
- To fill electric bulbs, hence reducing the rate of volatilisation of the tungsten filament.

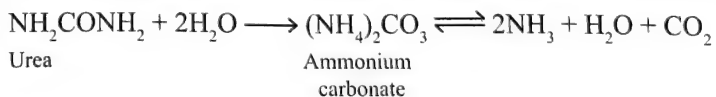
2.7.2 ACTIVE NITROGEN

Active nitrogen is made by passing an electric spark through N_2 gas at 2 mm pressure. This forms atomic nitrogen (N) and the process is associated with yellow-pink after glow. It decomposes many organic compounds.

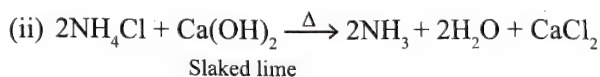
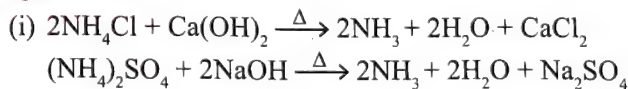


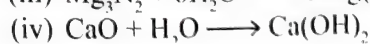
2.8 AMMONIA (NH_3)

Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter, e.g. urea



Preparation:



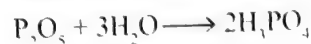


4. Ammonia cannot be dried by:

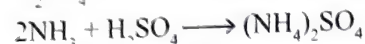
a. **Anhydrous CaCl_2 :** NH_3 forms a complex with CaCl_2 .



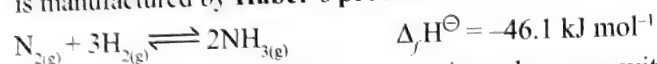
b. **Phosphorous pentoxide:** NH_3 reacts with P_2O_5 to form ammonium phosphate.



c. **Concentrated sulphuric acid:** NH_3 reacts with conc. H_2SO_4 to form ammonium sulphate.



5. **Manufacture of ammonia:** On commercial scale, ammonia is manufactured by **Haber's process**.



This reaction is reversible, exothermic and occurs with decrease in volume. In accordance with **Le Chatelier's principle**, the favourable conditions for the manufacture of ammonia are:

- Low temperature:** As the forward reaction is exothermic, low temperature will favour the formation of ammonia. The optimum temperature for the reaction has been found to be $\sim 700 \text{ K}$.
- High pressure:** As the forward reaction occurs with decrease in volume, high pressure will favour the formation of ammonia. The optimum pressure for the reaction is about $200 \times 10^5 \text{ Pa}$ or 200 atm .
- Catalyst:** Rate of reaction at 700 K and 200 atm pressure is increased by the use of catalyst such as iron oxide with small amount of K_2O and Al_2O_3 . Sometimes, molybdenum is used as a promoter (promoter increases the efficiency of the catalyst). Flow chart for the production of ammonia is given in Fig. 2.3.

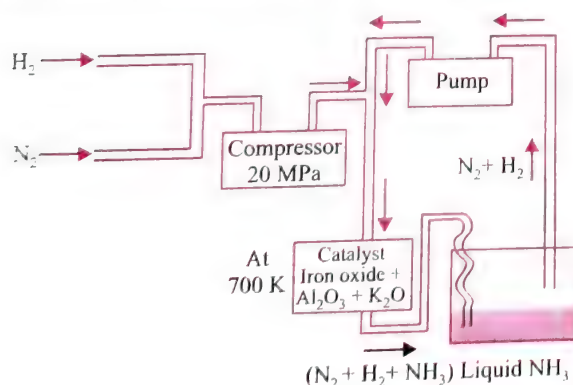


Fig. 2.3 Flow chart for the manufacture of NH_3 by Haber process

2.8.1 PROPERTIES

2.8.1.1 Physical Properties

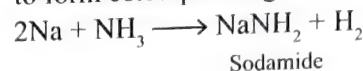
- Ammonia is a colourless gas with a characteristic pungent odour. It brings tears into the eyes.
- It is lighter than air (density = 0.68 g cm^{-3}).
- It is highly soluble in water. One volume of water dissolves 1300 volumes of ammonia at 0°C at 1 atm pressure. The high solubility in water is due to hydrogen bonding. The

solubility of ammonia increases with increase of pressure and decreases with increase of temperature.

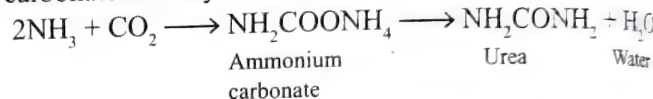
- It can be easily liquefied at room temperature by the application of pressure. Liquid ammonia is colourless and boils at 239.7 K and freezes at 198.4 K . In the solid and liquid state, it is associated through hydrogen bonds as in the case of water that accounts for its higher boiling and melting points than expected in comparison to other group 15 hydrides, on the basis of its molecular mass.
- On vapourisation, liquid ammonia causes intense cooling.

2.8.1.2 Chemical Properties

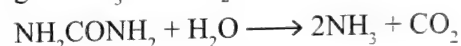
1. **Reaction with metals:** Ammonia reacts with Na or K metal to form corresponding amides and hydrogen is liberated.



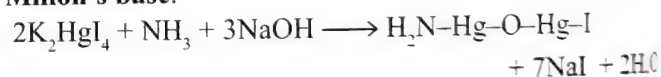
2. **Reaction with CO_2 :** Liquid NH_3 reacts with gaseous CO_2 at $453\text{--}473 \text{ K}$ and 220 atmospheres to form ammonium carbonate initially which further decomposes to give urea.



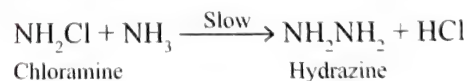
Urea is used as fertiliser as it decomposes slowly in soil to give NH_3 and CO_2 .



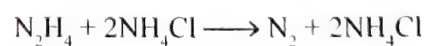
3. **Reaction with Nessler's reagent (test for ammonia):** Ammonia or ammonium salts reacts with Nessler's reagent to give a brown ppt. due to the formation of **iodide of Millon's base**.



4. **Reaction with sodium hypochlorite:** When an excess of ammonia solution is boiled with sodium hypochlorite, NaOCl in presence of glue or gelatin, hydrazine is formed.



Glue or gelatin catalyses the slow reaction and prevents the side reaction of the oxidation of hydrazine to nitrogen.



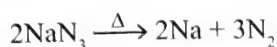
Uses:

- To produce various nitrogenous fertilisers such as ammonium nitrate, urea, ammonium phosphate, ammonium sulphate, calcium ammonium nitrate (CAN) etc.
- In the manufacture of some inorganic nitrogen compounds such as nitric acid (**in Ostwald's process**).
- As a cleansing agent for removing grease.
- Liquid ammonia is used as a refrigerant.
- As a laboratory reagent.

ILLUSTRATION 2.6

- a. Write the reaction of thermal decomposition of sodium azide.
 b. Why does NH_3 act as a Lewis base?

Sol. a. Thermal decomposition of sodium azide, NaN_3 gives N_2 gas.



- b. Lone pair on N in NH_3 is present in one of the sp^3 hybridised orbital, due to the directional nature of lone-pair of electron on which is available for donation, NH_3 acts as a Lewis base.

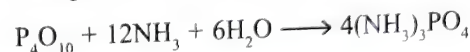
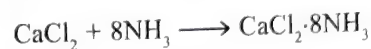
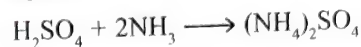
ILLUSTRATION 2.7

- a. A bottle of liquor ammonia should be cooled before opening. Give reason.
 b. Why conc. H_2SO_4 , anhydrous CaCl_2 and P_4O_{10} cannot be used as dehydrating agents for ammonia.

Sol.

- a. Liquor ammonia has high vapour pressure at room temperature. Hence, to reduce the vapour pressure inside the bottle in order to avoid bumping, it has to be cooled.

- b. Conc. H_2SO_4 , anhydrous CaCl_2 and P_4O_{10} react with ammonia and hence do not behave as dehydrating agent.

**2.9 OXIDES OF NITROGEN**

Oxides of nitrogen provide a fascinating picture from the point of view of their varied structures and diverse chemical behaviour. They range from N_2O , NO , N_2O_3 , NO_2 or N_2O_4 and N_2O_5 . The preparative routes for oxides of nitrogen and their properties are given in following Table 2.3.

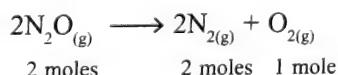
Table 2.3 Preparation and properties of oxides of nitrogen.

Name	Formula	Oxidation state of nitrogen	Preparation	Properties
Dinitrogen monoxide OR Nitrous oxide OR (Laughing gas)	N_2O	+1	1. $\text{NH}_4\text{NO}_3 \xrightarrow{250^\circ\text{C}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$ 2. $\text{NH}_2\text{OH} + \text{HNO}_2 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$ 3. $\text{Zn} + \text{dil. HNO}_3 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$	1. Colourless, neutral gas 2. In solid state, exist as $\text{N}_2\text{O} \cdot 6\text{H}_2\text{O}$ 3. $2\text{N}_2\text{O} \xrightarrow{600^\circ\text{C}} 2\text{N}_2 + \text{O}_2$
Nitrogen monoxide or Nitric oxide	NO	+2	1. $\left[\text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^- \right]$ $3e^- + \text{NO}_3^- \longrightarrow \text{NO}$ $3\text{Cu} + 8\text{HNO}_3(\text{dil}) \longrightarrow 2\text{NO} + 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O}$ 2. Catalytic oxidation of NH_3 $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}$	1. Colourless gas, solid and liquid NO is blue in colour. 2. $2\text{NO} \xrightarrow{1100^\circ\text{C}} \text{N}_2 + \text{O}_2$ 3. $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$
Dinitrogen trioxide	N_2O_3	+3	1. $\text{NO} + \text{NO}_2 \longrightarrow \text{N}_2\text{O}_3$ 2. $\text{As}_2\text{O}_3 + \text{HNO}_3(\text{dil}) + 2\text{H}_2\text{O} \longrightarrow \text{N}_2\text{O}_3 + 2\text{H}_3\text{AsO}_4$	1. In solid and liquid state N_2O_3 is blue in colour. In gaseous state, N_2O_3 completely dissociates to give NO and NO_2 . $\text{N}_2\text{O}_{3(\text{g})} \longrightarrow \text{NO} + \text{NO}_2$ 2. In conc. H_2SO_4 , blue colour disappears due to formation of nitrosonium hydrogen sulphate. $\text{N}_2\text{O}_3 + \text{H}_2\text{SO}_4(\text{conc.}) \longrightarrow 2\text{NO}^+ + 3\text{HSO}_4^- + \text{H}_3\text{O}^+$ 3. In presence of moisture, blue colour disappears due to formation of nitrous acid. $\text{N}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_2$ Hence in aqueous medium N_2O_3 is acidic in nature.

Nitrogen dioxide	NO ₂	+4	$\left[\begin{array}{l} \text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^- \\ \text{NO}_3^- + e^- \longrightarrow \text{NO}_2 \end{array} \right]$ <ol style="list-style-type: none"> 1. $\text{Cu} + 4\text{HNO}_3(\text{conc.}) \longrightarrow 2\text{NO}_2 + \text{Cu}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$ 2. $\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$ (LiNO₃ and Mg(NO₃)₂ also give same reaction.) 3. $\text{NO} + \text{O}_2 \longrightarrow \text{NO}_2$ 	<ol style="list-style-type: none"> 1. NO₂ is a brown gas, highly reactive and paramagnetic. 2. Acts as an oxidising agent $2\text{Cu} + \text{NO}_2 \longrightarrow \text{CuO} + \text{NO}$ $2\text{C} + 2\text{NO}_2 \longrightarrow 2\text{CO}_2 + \text{N}_2$ $\text{X}_2 + 2\text{NO}_2 \longrightarrow 2\text{XNO}_2$ (X = Cl, Br) 3. With strong oxidising agents, higher oxides of N are formed. $\text{O}_3 + 2\text{NO}_2 \longrightarrow \text{N}_2\text{O}_5 + \text{O}_2$
Nitrogen tetroxide	N ₂ O ₄	+4	$2\text{NO}_2 \xrightleftharpoons[\Delta]{\text{Cooling}} \text{N}_2\text{O}_4$	<ol style="list-style-type: none"> 1. $\text{N}_2\text{O}_4 + \text{H}_2\text{O} \longrightarrow \text{HNO}_2 + \text{HNO}_3$ 2. $\text{N}_2\text{O}_4 + \text{H}_2\text{SO}_4(\text{conc.}) \longrightarrow \text{NO}^+\text{HSO}_4^- + \text{HNO}_3$ 3. Exists in equilibrium with NO both in gaseous and liquid state.
Dinitrogenpentoxide	N ₂ O ₅	+5	<ol style="list-style-type: none"> 1. $2\text{HNO}_3 + \text{P}_2\text{O}_5 \longrightarrow 2\text{HPO}_3 + \text{N}_2\text{O}_5$ 2. $4\text{AgNO}_3 + 2\text{Cl}_2 \longrightarrow 4\text{AgCl} + 2\text{N}_2\text{O}_5 + \text{O}_2$ 	<ol style="list-style-type: none"> 1. In solid state, exist as a crystalline ionic compound, [NO₂]⁺ [NO₃]⁻ i.e. nitronium nitrate In gaseous state, exist as N₂O₅ having as oxygen bridge, N–O–N 2. In solid or gaseous state exist as $2\text{N}_2\text{O}_5 \longrightarrow 2\text{N}_2\text{O}_4 + \text{O}_2$ 3. $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_3$ That is why N₂O₅ is also known as anhydride of HNO₃. Hence it is acidic in nature.

2.9.1 DINITROGEN MONOXIDE OR NITROGEN (I) OXIDE (N₂O)

N₂O acts as better supporter of combustion than air. Reason being, in air % of O₂ is ≈ 22%, while N₂O decomposes to give ≈ 33% of O₂.



When inhaled in small amounts, N₂O induces intoxication and hysterical excitement often accompanied by convulsion laughter hence it is also known as **Laughing gas**. In large amounts, it acts as a narcotic. It is also used as an anaesthetic particularly in dentistry and gynaecology.

2.9.2 DINITROGEN OXIDE OR NITRIC OXIDE (NO)

Despite being odd electron the molecule is colourless. This can be explained on the basis of its electronic configuration.

NO (7 + 8 = 15 electrons)

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \pi 2p_y^2 = \pi 2p_x^2 < \pi^* 2p_y^1 < \pi^* 2p_x^0 < \sigma^* 2p_z^0$$

For NO to be coloured, transition from $\pi^* 2p \longrightarrow \sigma^* 2p$ is required which is forbidden, hence NO is colourless.

$$\text{B.O. of NO} = 1/2 (\text{N}_b - \text{N}_a) = 1/2 (10 - 5) = 2.5$$

NO⁺ will be more stable than NO molecule, as

$$\text{B.O. (NO}^+) = 1/2 (10 - 4) = 3.0$$

Bond order (B.O.) ∝ Stability

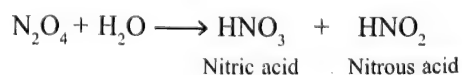
Greater the bond order, greater is the stability of the molecule.

In spite of its reactive and harmful nature, NO occurs in biological system in traces. **It acts as a neurotransmitter and plays a significant role in controlling blood pressure by relaxing blood vessels. It also provides protection from bacterial infections.**

Nitric oxide and nitrogen dioxide are important in the manufacture of nitric acid and nitrate fertilisers.

2.9.3 N₂O₄

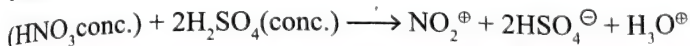
N₂O₄ is mixed anhydride of HNO₃ and HNO₂ as on reaction with water, N₂O₄ gives HNO₃ and HNO₂.



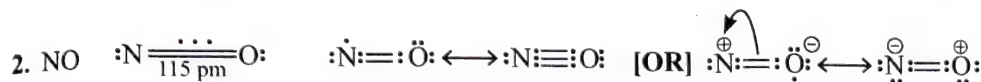
N₂O₄ is used as an oxidiser for rocket fuels in missiles and space vehicles.

2.9.4 NITRONIUM ION (NO_2^+)

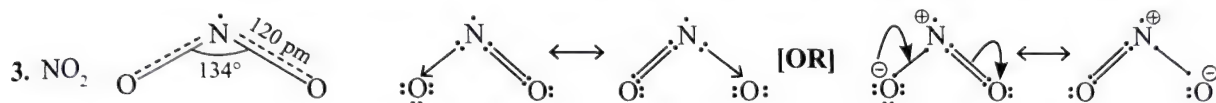
It is an active electrophilic species present in the mixtures of conc. H_2SO_4 and conc. HNO_3 used as a nitrating mixture in organic chemistry.



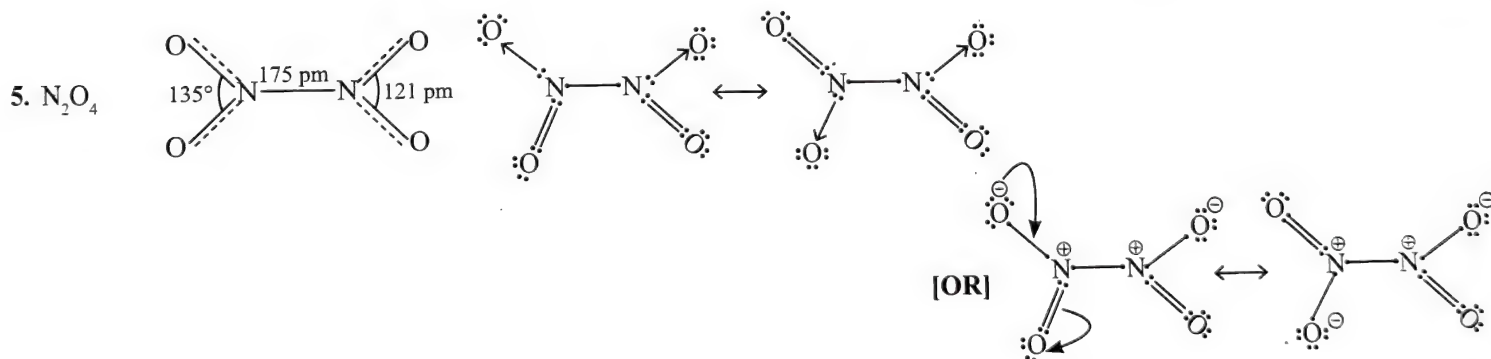
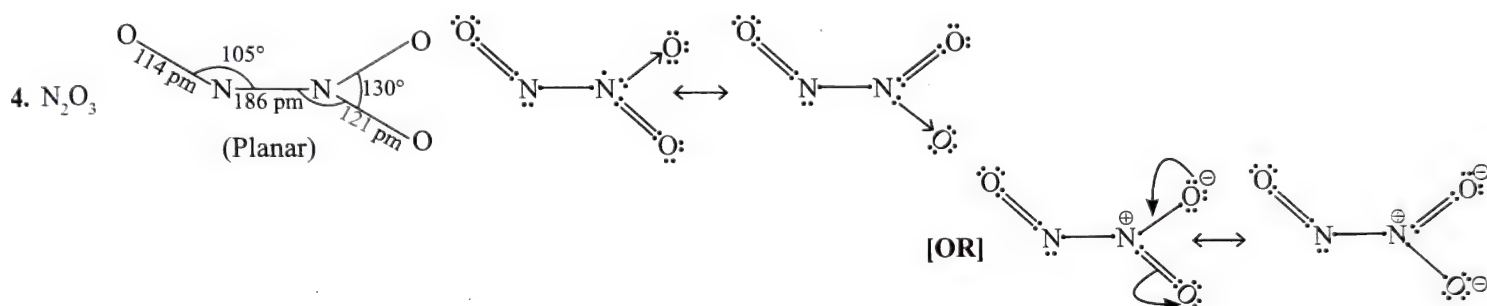
2.9.5 RESONATING STRUCTURE OF NITROGEN OXIDES



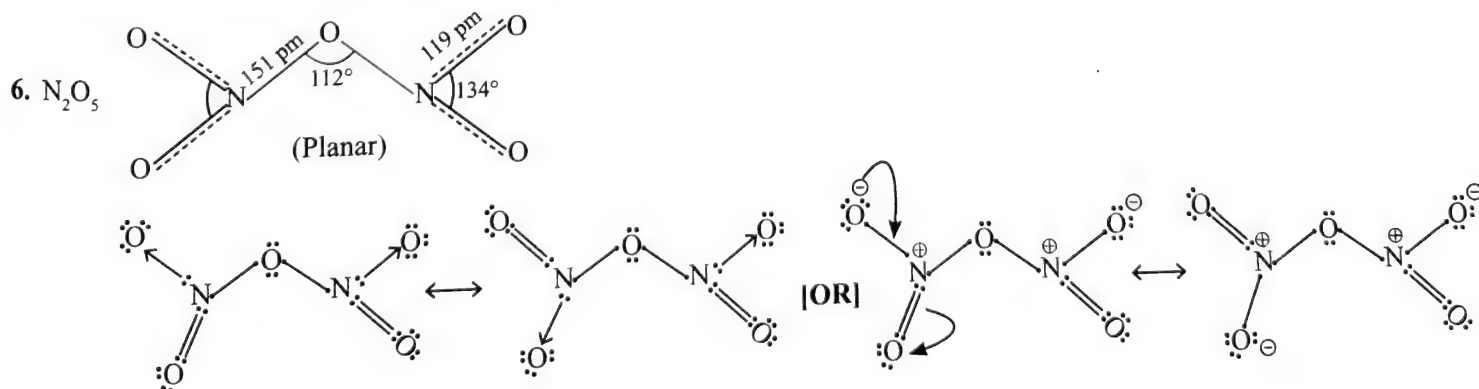
[Linear, $3e^-$ bond, paramagnetic in gaseous state. Diamagnetic in solid and liquid state due to dimerisation]



[Odd electron, paramagnetic. Dimerises on cooling to N_2O_4 .]



(Diamagnetic, dissociate on heating to NO_2)



[Solid N_2O_5 exists as $[\text{NO}_2]^+ [\text{NO}_3]^-$ and is called nitronium nitrate]

Fig. 2.4 Resonating structures of oxides of nitrogen

2.10 NITRIC ACID (HNO₃)

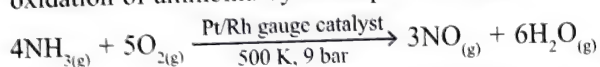
Nitric acid was named **aqua fortis** (meaning strong water) by Alchemists.

2.10.1 PREPARATION

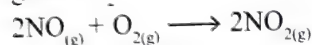
1. **In the laboratory:** Nitric acid is prepared by heating KNO₃ or NaNO₃ and concentrated H₂SO₄ in glass apparatus since HNO₃ attacks rubber and cork.



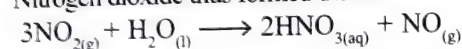
2. **On commercial scale:** It is manufactured mainly by **Ostwalds process**. This method is based upon the catalytic oxidation of ammonia by atmospheric oxygen.



Nitric oxide thus formed readily combines with oxygen to give NO₂.



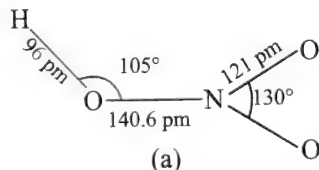
Nitrogen dioxide thus formed dissolves in water to form HNO₃.



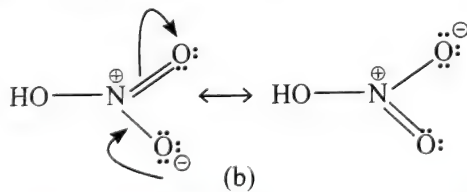
The nitric oxide thus formed is recycled and the aqueous HNO₃ is concentrated by distillation to give 68% HNO₃ by mass. (HNO₃ forms azeotrope at 68% HNO₃ and 32% water both by mass). Further concentration to 98% can be achieved by dehydration with concentrated H₂SO₄.

2.10.2 STRUCTURE

Spectroscopic studies have shown that in the gaseous state, HNO₃ exists as a planar molecule.



Nitric acid is a resonance hybrid of following:



2.10.5 REACTION OF DIFFERENT ELEMENT WITH HNO₃

These are summarised in Table 2.4.

Table 2.4 Reactions of different elements with HNO₃

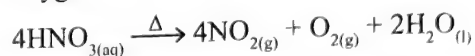
Different concentration of nitric acid	Element	Main products
Conc. HNO ₃ (NO ₃ [⊖] + 2H [⊕] + e [⊖] → NO ₂ + H ₂ O) (‘n’ factor = 1)	Cu, Ag, Hg, Pb, Zn	Metal nitrate + NO ₂
	Fe, Al, Co, Ni, Cr	Rendered passive
	Sn	Metastannic acid or hydrated stannic oxide (H ₂ SnO ₃) and NO ₂
Moderately conc. HNO ₃	Fe	Ferric nitrate and NO ₂
Dilute HNO ₃ (4H [⊕] + NO ₃ [⊖] + 3e [⊖] → NO + 3H ₂ O) (‘n’ factor = 3)	Cu, Ag, Hg, Pb	Metal nitrates and NO
	a. More active metals with dil. HNO ₃ like Zn, Fe, Sn b. 2NO ₃ [⊖] + 10H [⊕] + 8e [⊖] → N ₂ O + 5H ₂ O (‘n’ factor = 8/2 = 4)	Metal nitrates and N ₂ O

2.10.3 PHYSICAL PROPERTIES

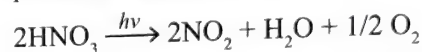
1. Pure HNO₃ is colourless liquid with pungent odour (freezing point 231.4 K and boiling point 355.6 K). However, impure HNO₃ is yellow due to the presence of dissolved NO₂.
2. Laboratory grade HNO₃ contains ~ 68% of the HNO₃ by mass and has specific gravity of 1.504.
3. **Fuming nitric acid** is pure nitric acid with dissolved NO₂ in it.

2.10.4 CHEMICAL PROPERTIES

1. On heating, HNO₃ decomposes to give nitrogen dioxide, oxygen and water.



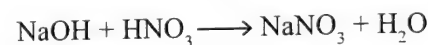
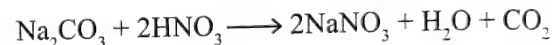
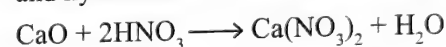
2. Nitric acid is stored in brown coloured glass bottles, to prevent photochemical decomposition of HNO₃.



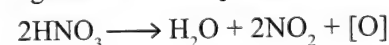
3. HNO₃ behaves as strong monobasic acid and ionises as follows:



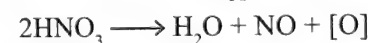
It reacts with basic oxides, carbonates, bicarbonates and hydroxides to form corresponding salts.



4. **Oxidising nature:** Nitric acid acts as strong oxidising agent as it decomposes to give nascent oxygen easily.



or



Most of the metals except noble metals like Au and Pt react with HNO₃. Some metals like Fe, Al, Co, Ni and Cr do not dissolve in conc. HNO₃ because of the formation of a layer of oxide on the metal surface, thus these metals are rendered passive.

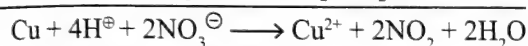
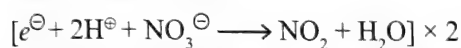
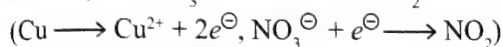
1. Very dil. HNO_3 $10\text{H}^{\oplus} + 8\text{e}^{\ominus} + \text{NO}_3^{\ominus} \longrightarrow \text{NH}_4^{\oplus} + 3\text{H}_2\text{O}$ (‘n’ factor = 8)	More active metals Zn, Fe, Sn	Metal nitrates and hydroxylamine (NH_2OH) or NH_4^{\oplus} ion or ammonium nitrate (NH_4NO_3)
2. Cold dil. HNO_3 $7\text{H}^{\oplus} + 6\text{e}^{\ominus} + \text{NO}_3^{\ominus} \longrightarrow \text{NH}_2\text{OH} + 2\text{H}_2\text{O}$ (‘n’ factor = 6)	Mg, Mn	Metal nitrates and H_2
Aqua regia (conc. HCl : conc. $\text{HNO}_3 = 3:1$)	Noble metals like Au, Pt	Complex ions such as $[\text{AuCl}_4]^{-}$, $[\text{PtCl}_6]^{2-}$ and $\text{NO}_{(\text{g})}$

Note: ‘n’ factor for different concentration of HNO_3

1. As an acid: $\text{HNO}_3 \longrightarrow \text{H}^{\oplus}$ ($n = 1$)
2. Conc. HNO_3 ($\text{NO}_3^{\ominus} \longrightarrow \text{NO}_2$) ($n = 1$)
3. Dilute HNO_3 ($\text{NO}_3^{\ominus} \longrightarrow \text{NO}$) ($n = 3$)
4. Dilute HNO_3 + to give N_2O with Zn, Fe, Sn. ($\text{NO}_3^{\ominus} \longrightarrow \text{N}_2\text{O}$) ($n = 4$)
5. Cold dil. HNO_3 ($\text{NO}_3^{\ominus} \longrightarrow \text{NH}_2\text{OH}$) ($n = 6$)
6. Very dil. HNO_3 ($\text{NO}_3^{\ominus} \longrightarrow \text{NH}_4^{\oplus}$) ($n = 8$)

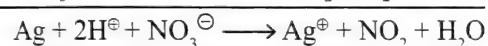
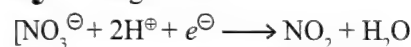
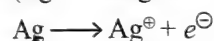
(A) Reactions with conc. HNO_3

- i. Cu, Ag, Hg, Pb, Zn react with conc. HNO_3 to form metal nitrates, and NO_3^{\ominus} is reduced to NO_2 .



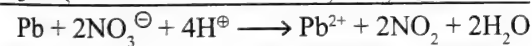
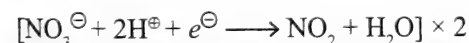
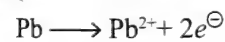
Add 2NO_3^{\ominus} ion to both sides to get molecular equation
or $\text{Cu} + 4\text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$

- ii. ($\text{Ag} \longrightarrow \text{Ag}^{\oplus} + \text{e}^{\ominus}$, $\text{NO}_3^{\ominus} + \text{e}^{\ominus} \longrightarrow \text{NO}_2$)



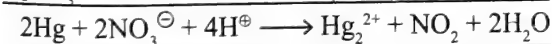
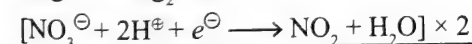
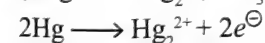
Add 2NO_3^{\ominus} ion to both sides to get molecular equation
or $\text{AgNO}_3 + 2\text{HNO}_3 \longrightarrow \text{AgNO}_3 + \text{NO}_2 + \text{H}_2\text{O}$

- iii. ($\text{Pb} \longrightarrow \text{Pb}^{2+} + 2\text{e}^{\ominus}$, $\text{NO}_3^{\ominus} + \text{e}^{\ominus} \longrightarrow \text{NO}_2$)



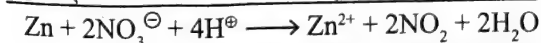
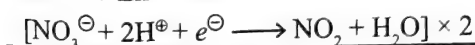
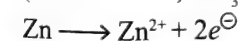
Add 2NO_3^{\ominus} ion to both sides to get molecular equation
or $\text{Pb} + 4\text{HNO}_3 \longrightarrow \text{Pb}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$

- iv. ($2\text{Hg} \longrightarrow \text{Hg}_2^{2+}$, $\text{NO}_3^{\ominus} \longrightarrow \text{NO}_2$)



Add 2NO_3^{\ominus} ion to both sides to get molecular equation
or $2\text{Hg} + 4\text{HNO}_3 \longrightarrow \text{Hg}_2(\text{NO}_3)_2 + 2\text{NO} + 2\text{H}_2\text{O}$

- v. ($\text{Zn} \longrightarrow \text{Zn}^{2+}$, $\text{NO}_3^{\ominus} \longrightarrow \text{NO}_2$)

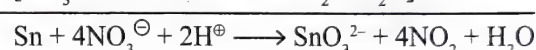
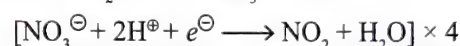
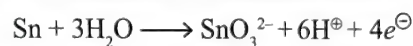


Add 2NO_3^{\ominus} ion to both sides to get molecular equation
or $\text{Zn} + 4\text{HNO}_3 \longrightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$

- (B) Fe, Al, Co, Ni and Cr are rendered passive with conc. HNO_3 . The inertness exhibited by metals under conditions in which chemical activity is expected is known as passivity. A thin

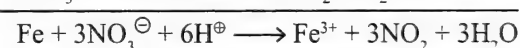
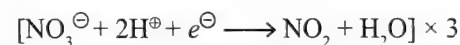
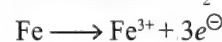
layer of oxide is formed on Fe, Al, Co, Ni and Cr with conc. HNO_3 , which prevents the further action of conc. HNO_3 .

- (C) Sn is oxidised to metastannic acid



Add 2H^{\oplus} ion to both sides to get molecular equation
or $\text{Sn} + 4\text{HNO}_3 \longrightarrow \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{H}_2\text{O}$

- (D) With moderately conc. H_2SO_4 , Fe gives ferric nitrate, HNO_3 is reduced to NO_2 .

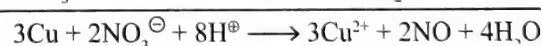
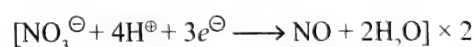


Add 3NO_3^{\ominus} ion to both sides to get molecular equation
or $\text{Fe} + 6\text{HNO}_3 \longrightarrow \text{Fe}(\text{NO}_3)_3 + 3\text{NO}_2 + 3\text{H}_2\text{O}$

(E) With dil HNO_3 :

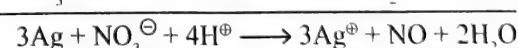
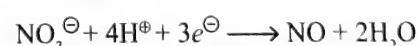
- I. Cu, Ag, Hg, Pb reacts with dil. HNO_3 to give metal nitrate and HNO_3 is reduced to NO.

- i. $[\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{e}^{\ominus}] \times 2$



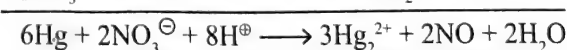
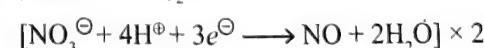
Add 6NO_3^{\ominus} ion to both sides to get molecular equation
or $3\text{Cu} + 8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$

- ii. $[\text{Ag} \longrightarrow \text{Ag}^{\oplus} + \text{e}^{\ominus}] \times 3$

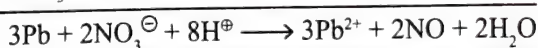
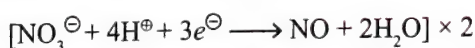


Add 3NO_3^{\ominus} ion to both sides to get molecular equation
or $3\text{Ag} + 4\text{HNO}_3 \longrightarrow 3\text{AgNO}_3 + \text{NO} + 2\text{H}_2\text{O}$

- iii. $[2\text{Hg} \longrightarrow \text{Hg}_2^{2+} + 2\text{e}^{\ominus}] \times 3$

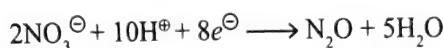
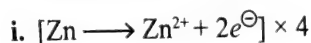


Add 6NO_3^{\ominus} ion to both sides to get molecular equation
or $6\text{Hg} + 8\text{HNO}_3 \longrightarrow 3\text{Hg}_2(\text{NO}_3)_2 + 2\text{NO} + 2\text{H}_2\text{O}$

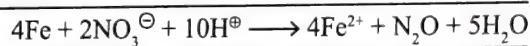
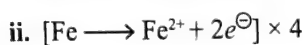


Add 6NO_3^- ion to both sides to get molecular equation
or $3\text{Pb} + 8\text{HNO}_3 \longrightarrow 3\text{Pb}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$

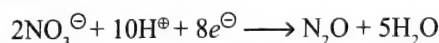
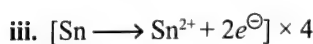
II. Zn, Fe, and Sn reacts with dil. HNO_3 to form metal nitrates and HNO_3 is reduced to N_2O .



Add 8NO_3^- ion to both sides to get molecular equation
or $4\text{Zn} + 10\text{HNO}_3 \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$



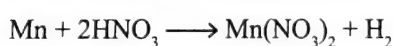
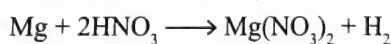
Add 8NO_3^- ion to both sides to get molecular equation
or $4\text{Fe} + 10\text{HNO}_3 \longrightarrow 4\text{Fe}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$



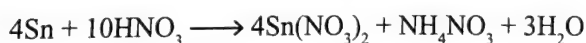
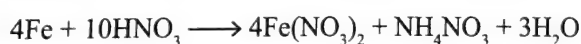
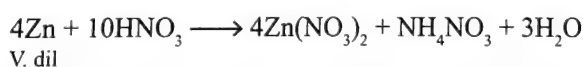
Add 8NO_3^- ion to both sides to get molecular equation
or $4\text{Sn} + 10\text{HNO}_3 \longrightarrow 4\text{Sn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$

(F) With very dil. HNO_3 :

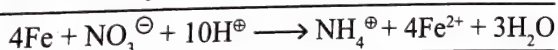
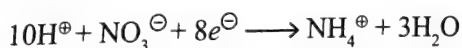
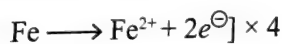
i. Mg and Mn liberate H_2



ii. Zn, Fe and Sn form metal nitrates and hydroxylamine or ammonium nitrate



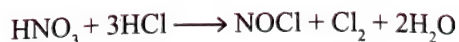
Ionic equation:



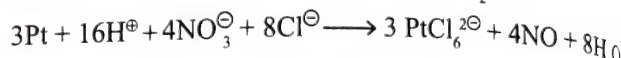
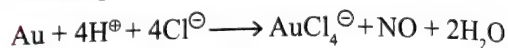
Add 9NO_3^- ion to both sides to get molecular equation.

Similarly, ionic equation for Sn and Zn can be written.

(G) Noble metals like gold, platinum, iridium, rhodium etc. do not react in HNO_3 . However, these metals dissolve in aqua regia (3 parts of conc. HCl and one part of conc. HNO_3) due to formation of chlorocomplexes such as AuCl_4^- , PtCl_6^{2-} etc.



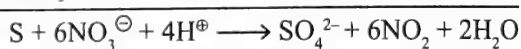
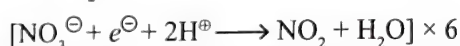
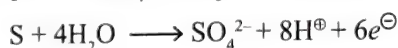
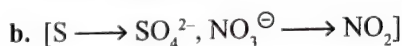
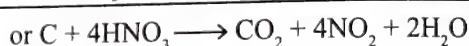
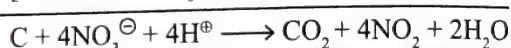
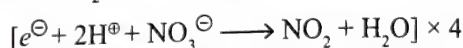
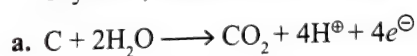
Ionic equations:



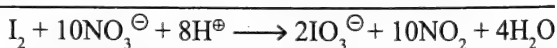
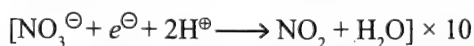
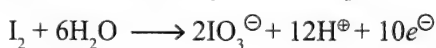
i. Cane sugar is oxidised to oxalic acid on reacting with HNO_3
 $\text{C}_{12}\text{H}_{22}\text{O}_{11} + 36\text{HNO}_3 \longrightarrow 6(\text{COOH})_2 + 36\text{NO}_2 + 23\text{H}_2\text{O}$

ii. Nitric acid reacts with proteins forming **xanthoprotein**, yellow nitro compound. It therefore stains skin and renders wool yellow. This property is used for the test of proteins.

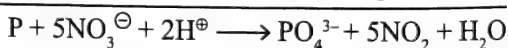
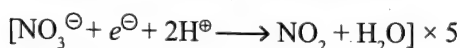
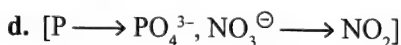
iii. **Oxidation of non-metals:** Dilute HNO_3 does not react with non-metals. But conc. HNO_3 oxidises non-metals such as C, S, I and metalloids such as As, Sb, etc. to their corresponding oxyacids, while nitric acid is reduced to NO_2 .



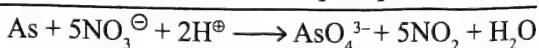
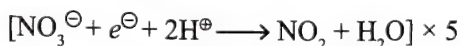
Add 2H^+ ion to both sides to get molecular equation
or $1/8 \text{S}_8 + 6\text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + 6\text{NO}_2 + 2\text{H}_2\text{O}$



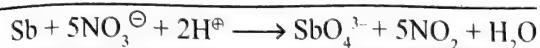
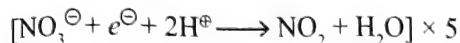
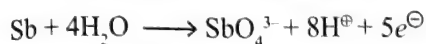
Add 2H^+ ion to both sides to get molecular equation
or $\text{I}_2 + 10\text{HNO}_3 \longrightarrow 2\text{HIO}_3 + 10\text{NO}_2 + 4\text{H}_2\text{O}$



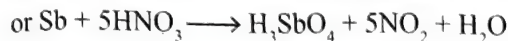
Add 3H^+ ion to both sides to get molecular equation
or $1/4 \text{P}_4 + 5\text{HNO}_3 \longrightarrow \text{H}_3\text{PO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}$



Add 3H^+ ion to both sides to get molecular equation
or $\text{As} + 5\text{HNO}_3 \longrightarrow \text{H}_3\text{AsO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}$



Add 3H^+ ion to both sides to get molecular equation

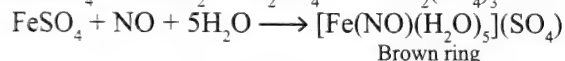
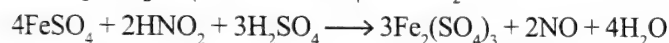
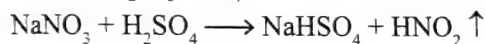


2.10.6 USES OF NITRIC ACID

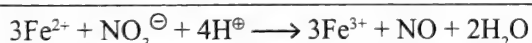
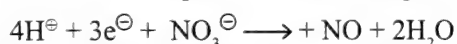
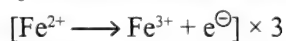
1. For purification of Au and Ag.
2. In the manufacture of TNT (trinitrotoluene), nitroglycerine and other organic nitro compounds.
3. In the pickling of stainless steel.
4. In etching of metals and as an oxidiser in rocket fuel.
5. In the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics.

2.10.7 TEST OF NITRATE ION (BROWN RING TEST)

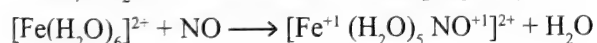
1. $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$ ion is formed in the brown ring test for the confirmation of nitrate ion in the salt analysis. To the nitrate solution, equal volume of freshly prepared saturated solution of FeSO_4 is added. To this solution, conc. H_2SO_4 is added slowly from the side of the test tube so that acid forms a layer beneath the mixture. A brown ring is formed at the junction of the two liquids, due to formation $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5](\text{SO}_4)$.



Ionic equations for NO_3^- ion test is represented as:-



$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is represented as $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$



Brown ring

2. The complex is paramagnetic ($n = 3$) and

$$\mu = \sqrt{15} = 3.83 \text{ BM.}$$

2.11 ALLOTROPY

Allotropy is the phenomenon by which an element exists in two or more different crystalline or amorphous forms; and the different forms are called allotropic forms or allotropes of the given element. Different allotropic forms of an element have different physical properties but similar chemical properties.

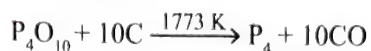
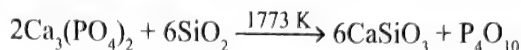
2.11.1 ALLOTROPIC FORMS OF PHOSPHOROUS

Phosphorous is found in various allotropic forms or modifications. Some important allotropes of phosphorous are:

1. White or yellow phosphorous
2. Red phosphorous
3. Black phosphorous

2.11.1.1 White Phosphorous

Preparation: On heating, phosphate rock, $\text{Ca}_3(\text{PO}_4)_2$ with coke and sand in an electric furnace at 1773 K, white or yellow phosphorous is obtained.



Structure: White phosphorous exists as tetrahedra tetraatomic discrete P_4 units (Fig. 2.10). The four phosphorous atoms are sp^3 hybridised and lie at the corners of the regular tetrahedron. Each phosphorous atom is linked to each of the other three atoms by covalent bonds. The P-P bond length is equal to 221 pm, and $\angle \text{PPP} = 60^\circ$. Due to high angular strain, white phosphorous is highly reactive.

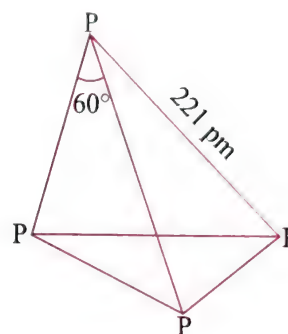


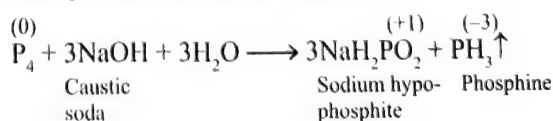
Fig. 2.5 Structure of white P_4

Property:

1. On exposure to light, white phosphorous turns yellow, hence it is also known as yellow phosphorous.
2. It is soft, translucent waxy solid with garlic odour. Being soft, it can be cut with a knife.
3. It is highly poisonous in nature. 0.15 g is the fatal dose. Persons working with phosphorous develop a disease in which the jaw bones decay and the disease is known as **phossy jaw**.
4. The various P_4 molecules are held together by weak van der Waals forces of attraction and hence the melting and boiling points of white phosphorous are quite low.
5. It is insoluble in water but readily dissolves in organic solvents such as CS_2 , alcohol and ether.
6. It contacts with air, it undergoes slow combustion and glows in dark. This property is called **phosphorescence**.
7. Its ignition temperature is low (about 30°C). It readily catches fire giving dense fumes of phosphorus pentoxide. It is, therefore, kept under water.

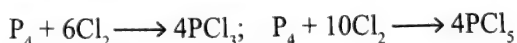


8. It dissolves in caustic alkalis on boiling in an inert atmosphere and forms phosphine.



It is an example of disproportionation reaction.

9. It directly combines with halogens forming first, trihalides and then pentahalides.



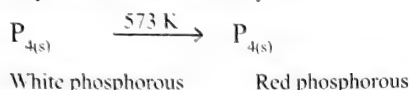
10. It combines with a number of metals forming phosphides.



11. It combines with sulphur with explosive violence forming a number of sulphides such as P_2S_3 , P_2S_5 , P_4S_3 and P_4S_7 .

2.11.1.2 Red Phosphorous

Preparation: It is obtained by heating white P_4 at 573 K in an inert atmosphere for several days.



Structure: Red phosphorous has polymeric structure, consisting of chains of P_4 tetrahedra linked together through covalent bonds (Fig. 2.6).

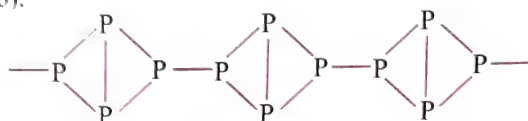
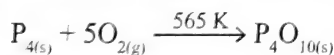


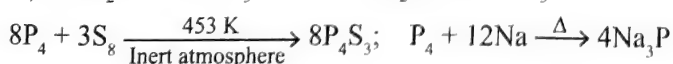
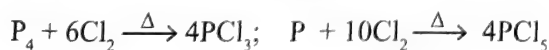
Fig. 2.6 Structure of red phosphorous

Property:

1. It is a hard crystalline odourless solid with iron grey lustre.
2. It is non-poisonous in nature.
3. It is insoluble in water as well in organic solvents such as CS_2 , alcohol and ether.
4. It is a relatively stable allotrope of phosphorus at room temperature. Its ignition temperature (543 K) is much higher than that of white phosphorus (303 K). Consequently, it does not catch fire easily.
5. It sublimes on heating giving vapours which are the same as given by white phosphorus. When these vapours are condensed, white phosphorus is obtained. Thus, red phosphorous is converted into white phosphorous.
6. It is denser (2.16 g cm^{-3}) than white phosphorous (1.84 g cm^{-3}) and is a bad conductor of electricity.
7. Being polymeric in nature, red phosphorous is less reactive than white phosphorus.
8. It burns in oxygen at 565 K to yield phosphorus pentoxide.



9. Being less reactive than white phosphorus, it reacts with halogens, sulphur and alkali metals only when heated forming their corresponding salts.

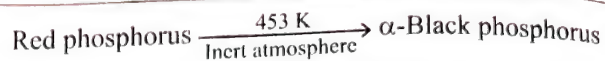


10. It does not react with caustic alkalis. This property is made use in separating, red phosphorus from white phosphorus.

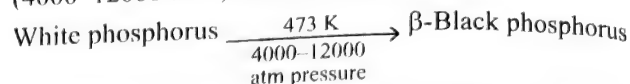
2.11.1.3 Black Phosphorous

It has two forms: α -black phosphorus and β -black phosphorus.

1. **Preparation:** α -black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K.



β -Black phosphorus (orthorhombic) is prepared by heating white phosphorus at 473 K under a very high pressure (4000–12000 atm.) in an inert atmosphere.



2. **Structure:** β -black phosphorus has a layered structure in which each phosphorus atom is covalently bonded to three neighbouring phosphorus atoms as shown in Fig. 2.7. The P—P—P angles are of 99° and P—P distance is 218 pm.

The adjacent layers are held 368 pm apart. The atoms within a layer are more strongly bound than the atoms in adjacent layers. This gives β -black phosphorus graphite like structure.

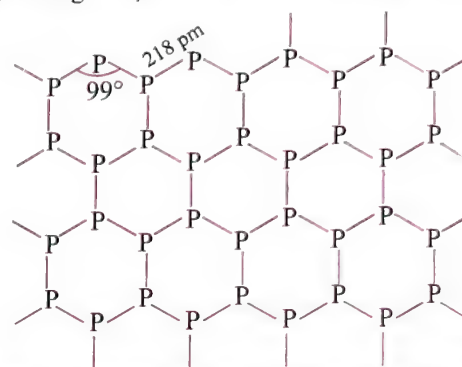


Fig. 2.7 Layered structure of β -black phosphorus

3. Properties:

- a. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals.
- b. It is a very stable allotrope of phosphorous and does not oxidise in air until heated very strongly.
- c. It is good conductor of electricity.

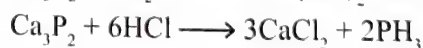
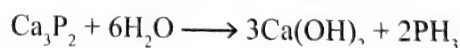
4. Uses:

- a. In the manufacture of food grade phosphates, detergent phosphates and pharmaceuticals.
- b. Elemental phosphorous is used in water industry.
- c. In the manufacture of organophosphorous compounds used as pesticides.
- d. In the form of phosphatic fertilisers in agriculture.

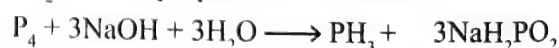
2.12 PHOSPHINE (PH_3)

Preparation:

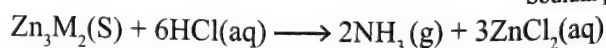
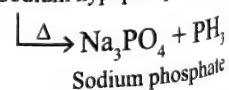
1. By hydrolysis of metal phosphides such as Ca_3P_2 or Na_3P with water or dilute HCl .



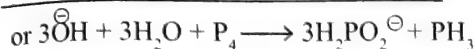
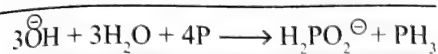
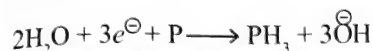
2. In laboratory, it is prepared by heating white phosphorous with concentrated NaOH solution in an inert atmosphere of CO_2 . It is disproportionation reaction.



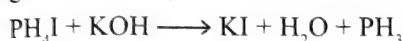
Phosphine (Sodium hypophosphite)



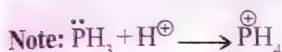
where $\text{M} = \text{As}, \text{Sb}$.

$$2\text{OH}^{\ominus} + 2\text{H}_2\text{O} + \text{P} \longrightarrow \text{H}_2\text{PO}_2^{\ominus} + e^{\ominus} + 2\text{H}_2\text{O}] \times 3$$


To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

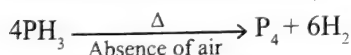

$$4\text{H}_3\text{PO}_3 \xrightarrow{\text{Heat}} 3\text{H}_3\text{PO}_4 + \text{PH}_3$$

Phosphorous acid Phosphoric acid Phosphine

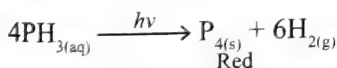


According to Drago's rule $1p$ e^- 's on P lie in almost pure s -orbital, hence due to non-directional nature, its overlapping tendency is less in comparison to a $1p$ e^- 's present in hybrid orbitals, which is direction as present NH_3 .

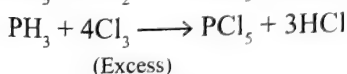
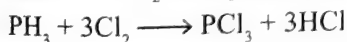
1. It is a colourless gas with rotten fish smell and is highly poisonous.
2. It is slightly soluble in water, the aqueous solution is neutral.
3. Phosphine decomposes on heating in absence of air into its constituent elements, i.e. P_4 and H_2 .



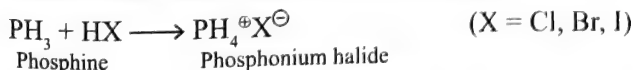
Solution of PH_3 in water decomposes in presence of light giving red phosphorous and H_2 .



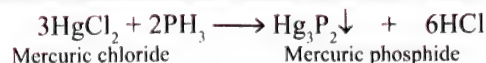
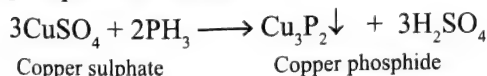
4. Phosphine explodes in contact with traces of oxidising agent like Cl_2 or Br_2 vapours, HNO_3 etc.



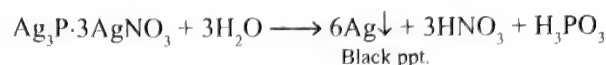
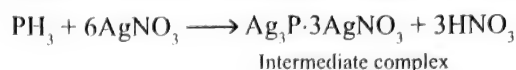
5. Phosphine is feebly basic and like NH_3 forms salts with mineral acids under anhydrous conditions.



6. When PH_3 is bubbled through the aqueous solutions of copper, and mercury salts, the precipitates of corresponding phosphides are formed.



7. With silver nitrate, first a complex of silver phosphide is produced, which is subsequently reduced in presence of water to metallic silver which appears as a black ppt.



1. **Spontaneous combustion of PH_3 .** It is used as Holme's signals in deep seas and oceans for signalling danger points to steamers. Containers containing a mixture of calcium phosphide and calcium carbide are pierced and thrown into the sea. In contact with water, a mixture of phosphine and acetylene gases is produced. Phosphine frequently contains traces of highly inflammable disphosphine P_2H_4 which catches fire spontaneously. This ignites acetylene which burns with a luminous flame and thus serves as a signal to the approaching ship. That is, PH_3 sometimes called cold fire.

2. Shells containing calcium phosphide are exploded by warships. Calcium phosphide reacts with water producing phosphine which burns in air to give clouds of P_4O_{10} which act as smoke screens.

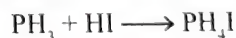
a. Why does NO_2 dimerise?

b. In what way can it be proved that PH_3 is basic in nature?

a. NO_2 contains odd number of valence electrons.

It behaves as an odd electron molecule hence it dimerises. On dimerisation, it is converted to stable N_2O_4 molecule with even number of electrons.

b. PH_3 reacts with acids like HI to form PH_4I which shows that it is basic in nature.



Due to lone pair of electrons on P in PH_3 , it acts as a Lewis base in the above reaction.

a. A tetraatomic molecule (A) on reaction with nitrogen (I) oxide, produces two substances (B) and (C). (B) is a dehydrating agent while substance (C) is a diatomic gas which shows almost inert behaviour. Identify (A), (B) and (C).

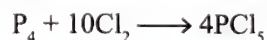
b. Why red phosphorous is denser and chemically less reactive than white phosphorous?

c. Why nitrous oxide supports combustion better than air?

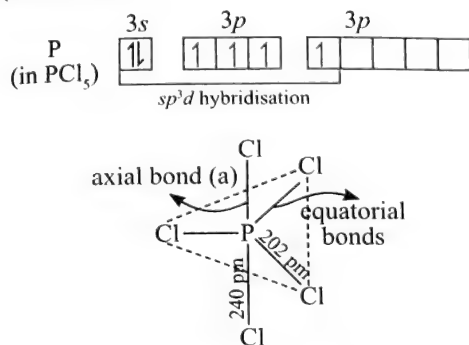
a.
$$\begin{array}{ccccc} \text{(A)} + \text{N}_2\text{O} & \longrightarrow & \text{(B)} + & \text{(C)} \\ \text{Tetraatomic} & & \text{Dehydrating} & & \text{Inert} \\ \text{molecule} & & \text{agent} & & \text{gas} \end{array}$$

$$\text{P}_4 + 10\text{N}_2\text{O} \longrightarrow \text{P}_4\text{O}_{10} + 10\text{N}_2$$

$$\begin{array}{ccccc} \text{(A)} & & \text{(B)} & & \text{(C)} \end{array}$$



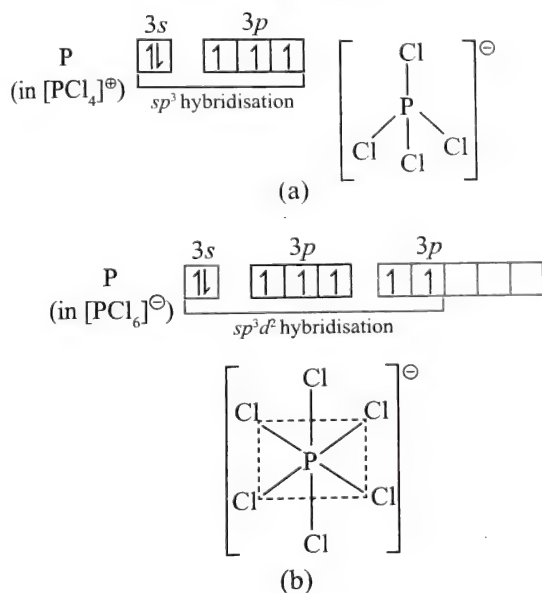
2. By the action of sulphuryl chloride, SO_2Cl_2 on white phosphorous.
- $$\text{P}_4 + 10\text{SO}_2\text{Cl}_2 \longrightarrow 4\text{PCl}_5 + 10\text{SO}_2$$
3. **Structure:** P in PCl_5 undergoes sp^3d hybridisation and PCl_5 has trigonal bipyramidal geometry in gaseous and liquid state (Fig. 2.8).

Fig. 2.8 Structure of PCl_5

The three equatorial P—Cl bonds are equivalent, while the two axial P—Cl bonds are equivalent and larger than equatorial bonds. $\angle\text{ClPCl}$ in equatorial plane is 120° , and in axial plane is 90° .

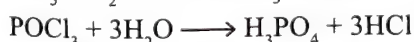
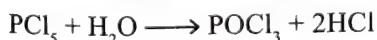
In the **solid state**, PCl_5 exists as an ionic solid

$[\text{PCl}_4]^+ [\text{PCl}_6]^-$ in which $[\text{PCl}_4]^+$ is tetrahedral while $[\text{PCl}_6]^-$ is octahedral. (Fig. 2.9(a) and (b))

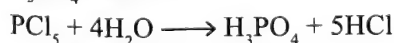
Fig. 2.9 (a) Structure of $[\text{PCl}_4]^+$ and (b) Structure of $[\text{PCl}_6]^-$

4. Properties:

- a. PCl_5 is a yellowish white crystalline solid with a characteristic smell.
- b. In moist air, it hydrolyses to POCl_3 and finally gets converted to phosphoric acid.

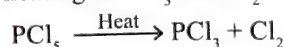


With excess of water, PCl_5 reacts violently to produce H_3PO_4 and HCl .

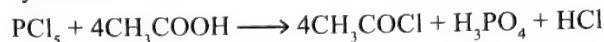


(Excess)

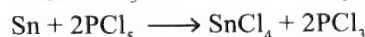
- c. On heating, it sublimes but decomposes on stronger heating to PCl_3 and Cl_2 .



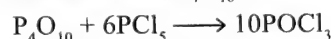
- d. PCl_5 converts carboxylic acids to acid chlorides and alcohols to alkyl halides, i.e. it is used in organic synthesis.



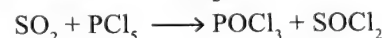
- e. PCl_5 reacts with finally divided metal on heating to give corresponding chlorides.



- f. Reaction with P_4O_{10} .



- g. Reaction with SO_2 .



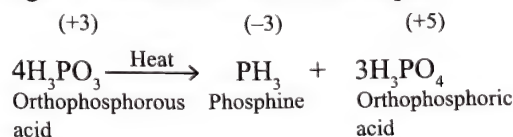
Thionyl chloride

2.14 OXOACIDS OF PHOSPHOROUS

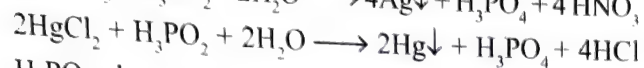
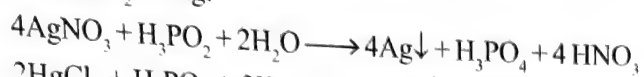
1. The oxoacids of nitrogen have no phosphorous analogues and although HPO_3 has the same empirical formula as HNO_3 , it is a polymeric compound unlike HNO_3 . The difference lies in the fact that strong $p\pi-p\pi$ bonding does not occur between phosphorous and oxygen. However, in all the oxyacids of phosphorous and their salts, the terminal P—O bonds are shorter than expected value for a P—O single bond, from which it is assumed that σ bonding between P and O is augmented by ($p\pi-d\pi$) bonding between empty $3d$ orbitals on P and filled $2p$ orbital on oxygen to give P—O linkages multiple bond character.

The phosphorous oxoacids can be divided into two classes:

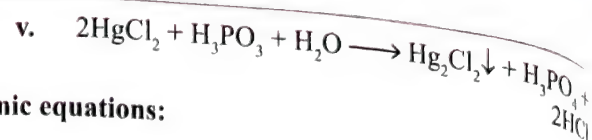
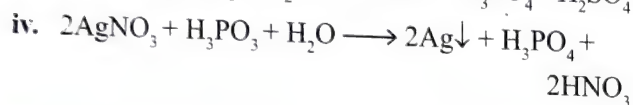
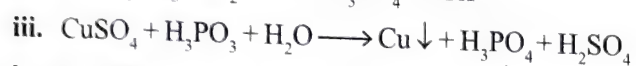
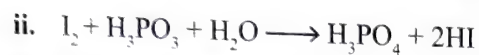
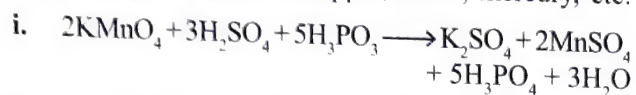
- a. Phosphorous acids, in which the formal oxidation state of P is +1 and +3.
- b. Phosphoric acids, in which the formal oxidation state of P is +5.
2. Few important points about oxoacids of phosphorous are as follows:
- a. In all oxoacids, phosphorous is tetrahedrally surrounded by four other atoms or groups.
- b. All these acids contain at least one P = O and one P—OH bond.
- c. The oxoacids in which phosphorus has oxidation state less than +5, contain, in addition to P = O and P—OH bonds, either P—H (e.g., H_3PO_2 , H_3PO_3) or P—P (e.g., $\text{H}_4\text{P}_2\text{O}_6$) bonds but not both.
- d. The oxoacids in +3 oxidation state undergo disproportionation reaction to give compounds in lower and higher oxidation states. For example



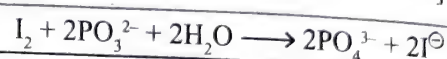
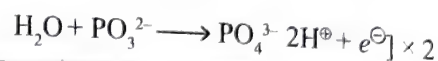
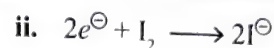
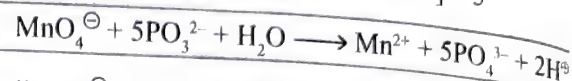
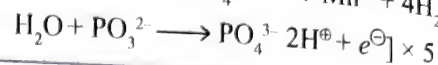
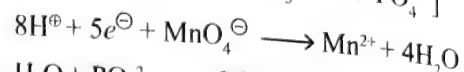
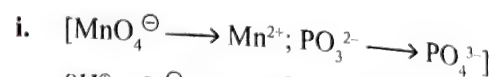
e. Acids which contain P—H bonds have behave as reducing agents. For example, hypophosphorous acid (H_3PO_2) is a good reducing agent as it contains two P—H bonds and thus reduces AgNO_3 to metallic silver and HgCl_2 to Hg .



H_3PO_3 also acts as a reducing agent though weaker than H_3PO_2 because it contains only one P—H bond as compared to two in H_3PO_2 . It reduces acidified KMnO_4 , I_2 , and salts of copper, silver, mercury, etc.



Ionic equations:



Similarly, the ionic equation for reaction (iii), (iv) and (v) can be written.

f. Oxoacids of phosphorous are summarised in Table 2.5

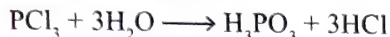
Table 2.5 Some oxoacids of phosphorous

	Name	Formula and O.S.	Characteristics bonds and their number	Basicity	Methods of preparation
1.	Orthophosphoric acid	H_3PO_4 (+5)	Three P—OH, one P=O	Tribasic	$\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} (\text{Excess}) \longrightarrow 4\text{H}_3\text{PO}_4$
2.	Peroxomonophosphoric acid	H_3PO_5 (+5)	Two P—OH, one P=O, one P—O—O—H	Tribasic	$\text{P}_4\text{O}_{10} + 4\text{H}_2\text{O}_2 (30\%) + 2\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{PO}_5$
3.	Orthophosphorous acid (Phosphonic acid)	H_3PO_3 (+3)	Two P—OH, one P—H, one P=O	Dibasic	$\text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{PO}_3$ $\text{PCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$
4.	Hypophosphorous acid (Phosphinic acid)	H_3PO_2 (+1)	One P—OH, two P—H, one P=O	Monobasic	$2\text{P}_4 + 3\text{Ba}(\text{OH})_2 + 6\text{H}_2\text{O} \longrightarrow 2\text{PH}_3 + 3\text{Ba}(\text{H}_2\text{PO}_2)_2$ $\text{Ba}(\text{H}_2\text{PO}_2)_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + 2\text{H}_3\text{PO}_2$ $\text{P}_4 + 3\text{NaOH} \longrightarrow 3\text{NaH}_2\text{PO}_2 + \text{PH}_3 + 3\text{H}_2\text{O}$
5.	Metaphosphoric acid (exists in polymeric form), e.g.,	HPO_3 (+5)	One P—OH, two P=O	Monobasic	$2\text{H}_3\text{PO}_4 \xrightarrow{520\text{ K}} \text{H}_4\text{P}_2\text{O}_7 \xrightarrow{870\text{ K}} 2\text{HPO}_3$
	Cyclotrimetaphosphoric acid	$(\text{HPO}_3)_3$ (+5)	Three P—OH, three P=O, three P—O—P	Tribasic	$3\text{H}_3\text{PO}_3 + 3\text{Br}_2 \xrightarrow[\text{Sealed tube}]{\Delta} (\text{HPO}_3)_3 + 6\text{HBr}$
	Linear polymetaphosphoric acid	$(\text{HPO}_3)_n$ (+5)	$n(\text{P}=\text{O})$, $n(\text{P}—\text{OH})$, $n(\text{P}—\text{O}—\text{P})$	Polybasic	$n\text{H}_3\text{PO}_4 \xrightarrow[316^\circ\text{C}]{\text{Heat}} (\text{HPO}_3)_n + n\text{H}_2\text{O}$
6.	Pyrophosphoric acid	$\text{H}_4\text{P}_2\text{O}_7$ (+5)	Four O—H, two P=O, one P—O—P	Tetrabasic	$2\text{H}_3\text{PO}_4 \xrightarrow{523\text{ K}} \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$
7.	Peroxodiphosphoric acid	$\text{H}_4\text{P}_2\text{O}_8$ (+5)	Four O—H, two P=O, one P—O—O—P	Tetrabasic	Electrolysis of a mixture of K_2HPO_4 + KF
8.	Pyrophosphorous acid	$\text{H}_4\text{P}_2\text{O}_5$ (+3)	Two P—OH, two P—H, two P=O, one P—O—P	Dibasic	$5\text{H}_3\text{PO}_3 + \text{PCl}_3 \longrightarrow 3\text{H}_4\text{P}_2\text{O}_5 + 3\text{HCl}$
9.	Hypophosphoric acid	$\text{H}_4\text{P}_2\text{O}_6$ (+4)	Four P—OH, two P=O, one P—P	Tetrabasic	$2\text{P}(\text{red}) + 4\text{NaOCl} + 2\text{H}_2\text{O} \longrightarrow \text{H}_4\text{P}_2\text{O}_6 + 4\text{NaCl}$

- Why does PCl_3 fume in moisture?
- Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.
- How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure?
- Give the disproportionation reaction of H_3PO_3 .

Sol.

- PCl_3 hydrolyses in the presence of moisture and gives fumes of HCl .

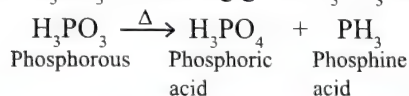


- All 5 bonds are not equivalent.

PCl_5 has trigonal bipyramidal geometry, the three P-Cl bonds in the equatorial plane have same bond length and two P-Cl bonds in the axial plane have same bond length. Axial P-Cl bonds are longer than equatorial P-Cl bonds.

- In H_3PO_2 , two H atoms are bonded directly to P atom, hence due to weak P-H bonds H_3PO_2 acts as a reducing agent.

- H_3PO_3 on heating gives H_3PO_4 and PH_3 .



CONCEPT APPLICATION EXERCISE 2.1

Subjective Type

- Write complete balanced reactions for the following:
 - Red phosphorous reacts with iodine in presence of water.
 - White phosphorous is boiled with a strong solution of NaOH in an inert atmosphere.
 - Phosphorous reacts with conc. HNO_3 to give H_3PO_4 .
 - Iodine reacts with concentrated nitric acid.
 - Orthophosphoric acid is heated with nitric acid and ammonium molybdate.
 - Disodium hydrogen phosphate is added to ammonical solution of magnesium sulphate.
 - Magnesium is burnt in air and the product is treated with water.
 - Phosphine is passed through AgNO_3 solution.
 - A mixture of air and ammonia is passed over heated platinum gauze.
 - Gold is treated with aqua regia.
 - Water is added to calcium phosphide.
 - Calcium phosphate is heated with a mixture of sand and carbon.
 - Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide.
 - Zinc is treated with very dilute nitric acid.
 - Phosphine is treated with an acidified CuSO_4 solution.

- Describe the action of heat on the following compounds:

- Ammonium nitrate
- Ammonium nitrite
- Ammonium chloride
- Ammonium dichromate
- Orthophosphoric acid
- Phosphrous acid
- Hypophosphorous acid
- Copper nitrate

- Complete and balance the following reactions:

- $\text{P}_4\text{O}_{10} + \text{PCl}_5 \longrightarrow$ _____
- $\text{NH}_3 + \text{NaOCl} \longrightarrow$ _____ + $\text{NaCl} + \text{H}_2\text{O}$
- $\text{Ca}(\text{PO}_4)_3 + 4\text{H}_3\text{PO}_4 \longrightarrow$ _____
- $\text{AgCl} + \text{NH}_4\text{OH} \longrightarrow$ _____ + _____
- $\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} \text{PbO} +$ _____ + _____
- $\text{Mg} + \text{HNO}_3 \longrightarrow$ _____ + _____

- In hyponitrous acid, If X is number of σ bonds, Y is the number of non-bonding electrons and Z is the number of π bonds. Then value of $(X + Y - \frac{Z}{2})$ is

- If the oxidation state of P in metaphosphate ion, dihydrogen hypophosphite ion and dihydrogen phosphite ion are X , Y and Z respectively. Then value of $\frac{X+Y+Z}{5}$ is

- In cyclotrimetaphosphoric acid $(\text{HPO}_3)_3$ if X is the number of $(p\pi - d\pi)$ multiple bonds, Y is the total number of sp^3 -hybridised atoms and Z is number of sp^2 -hybridised atoms. Then value of $\frac{X+Y-Z}{4}$ is

- In white or yellow phosphorous, calculate the value of expression $\frac{P+Q+R+S}{5}$.

If P = Atomicity of phosphorous,

Q = Total number of vertex angle in phosphorous molecular

R = Total number of P — P bond in phosphorous.

S = Total number of lone pairs in phosphorous molecule.

Solved Examples

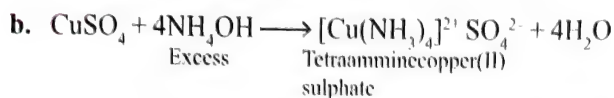
EXAMPLE 2.1

An aqueous solution of a gas (X) shows the following reactions:

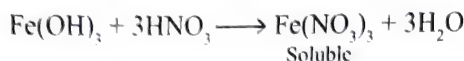
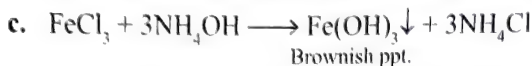
- It turns red litmus blue.
 - When added in excess to a copper sulphate solution, a deep blue coloured solution is obtained.
 - On addition to FeCl_3 solution, a brownish precipitate is formed, which is soluble in HNO_3 .
- Identify (X) and give an explanation for step (a), (b) and (c).

Sol. The gas (X) is ammonia, NH_3 .

a. Aqueous solution of NH_3 is NH_4OH , which is basic and hence turns red litmus blue.



$[\text{Cu}(\text{NH}_3)_4] \text{SO}_4$ is deep blue in colour and is soluble in water, hence deep blue coloured solution is formed.

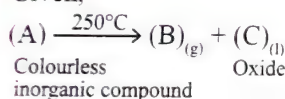


On addition of NH_4OH to FeCl_3 solution, brown ppt. of ferric hydroxide, $\text{Fe}(\text{OH})_3$ is formed. $\text{Fe}(\text{OH})_3$ dissolves in HNO_3 due to formation of ferric nitrate, $\text{Fe}(\text{NO}_3)_3$.

EXAMPLE 2.2

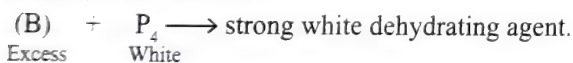
A colourless inorganic salt (A) decomposes completely at about 250°C to give only two products (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in this process.

Sol. Given,

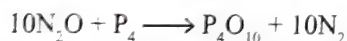
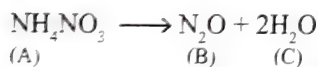


Liquid (C) is neutral oxide at room temperature and neutral to litmus paper.

Gas (B) is neutral oxide.



Both (B) and (C) are neutral oxides, (B) helps in combustion of white phosphorous, hence (B) can be nitrous oxide, N_2O . (C) is liquid at room temperature, hence it can be H_2O .



P_4O_{10} is strong white dehydrating agent.

(A) is ammonium nitrate, NH_4NO_3 , (B) is nitrous oxide, N_2O (C) is water, H_2O .

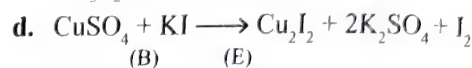
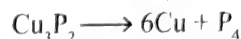
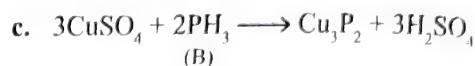
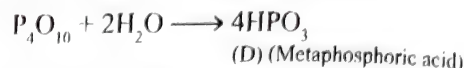
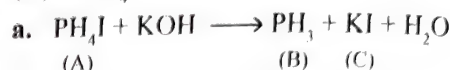
EXAMPLE 2.3

Identify (A) to (E).

- An inorganic iodide (A) on heating with a solution of KOH gives a gas (B) and the solution of a compound (C).
- The gas (B) on ignition in air gives a compound (D) and water.
- Copper sulphate is reduced to the metal on passing (B) through the solution.
- A precipitate of the compound (E) is formed on reaction of (C) with copper sulphate solution.

Sol. Gas (B) on ignition gives water, therefore hydrogen is present in the gas.

An inorganic iodide with alkali (KOH) gives a gas (B) an hydrogen compound, so (A) may be NH_4I or PH_4I . As NH_3 does not reduce CuSO_4 , therefore the compound (A) is PH_4I .

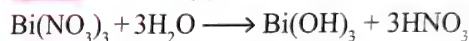


Hence (A) is PH_4I , (B) is PH_3 , (C) is KI , (D) is HPO_3 and (E) is Cu_2I_2 .

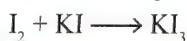
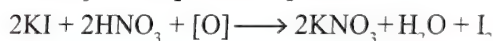
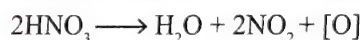
EXAMPLE 2.4

On gradual addition of KI solution to $\text{Bi}(\text{NO}_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Given an explanation for above observations.

Sol. $\text{Bi}(\text{NO}_3)_3$ undergoes hydrolysis to form HNO_3 .



HNO_3 reacts with KI to liberate I_2 , which dissolves in excess of KI giving clear yellow solution.



EXAMPLE 2.5

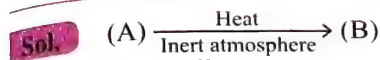
- A certain element is a metalloid that forms an acidic oxide E_2O_5 . Identify the element.
- N_2 makes up about 79% of the atmosphere, why do not animals use the more abundant N_2 instead of O_2 for the biological processes?

Sol.

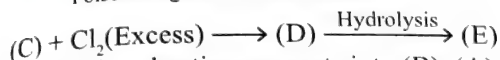
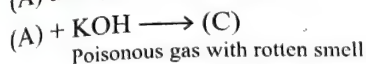
- Since the element forms an oxide with the formula E_2O_5 , it must be an element of group 15. Group 15 has two metalloids namely As and Sb. Acidic character of pentoxides of group 15 decreases down the group. Hence As_2O_5 is acidic and Sb_2O_5 is amphoteric. Thus the element is As and the metalloid is As_2O_5 .
- Large amount of energy is needed by the animals for their movement and to maintain the body temperature. Hence, to obtain the energy, it is much easier to break ($\text{O}=\text{O}$) bond rather than ($\text{N}\equiv\text{N}$) bond, since ($\text{O}=\text{O}$) bond is weaker as compared to $\text{N}\equiv\text{N}$ bond.

EXAMPLE 2.6

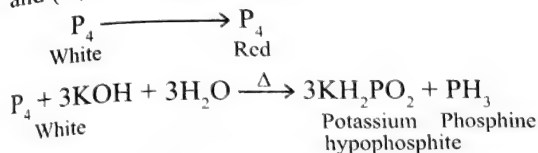
A translucent white waxy solid (A) on heating in an inert atmosphere is converted into its allotropic form (B). (A) on reaction with very dilute KOH liberates a highly poisonous gas (C), having rotten smell. With excess of chlorine, (C) forms (A) which hydrolyses to compound (E). Identify (A) to (E).



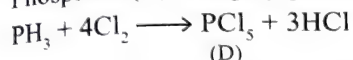
(A) and (B) are allotropes.



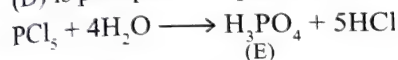
Since (A) on heating converts into (B), (A) is white phosphorous and (B) is red phosphorous.



Phosphine (C) is highly poisonous gas.



(D) is phosphorous pentachloride.

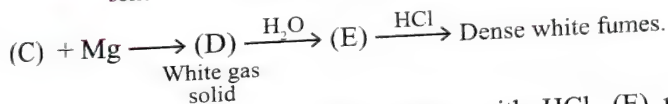
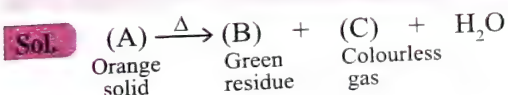


(E) is phosphoric acid.

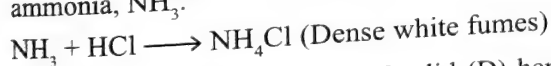
Hence (A) is white phosphorous, (B) is red phosphorous, (C) is phosphine, (D) is phosphorous pentachloride, (E) is phosphoric acid.

EXAMPLE 2.7

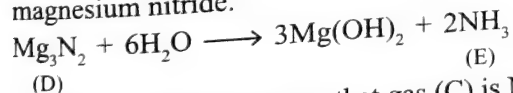
An orange solid (A) on heating gave a green residue (B), a colourless gas (C) and water vapour. The dry gas (C) on passing over heated magnesium gave a white solid (D). (D) on reaction with water gave a gas (E) which formed dense white fumes with HCl. Identify (A) to (E) and give the reactions.



Since (E) forms dense white fumes with HCl, (E) must be ammonia, NH₃.

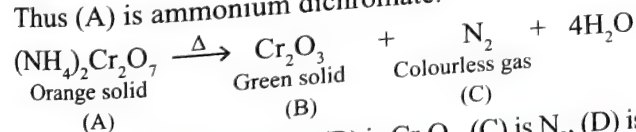


NH₃ is formed by hydrolysis of solid (D) hence, (D) is Mg₃N₂, magnesium nitride.



Formation of (D) indicates that gas (C) is N₂.

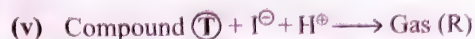
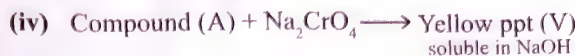
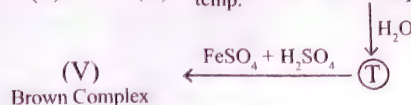
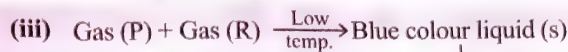
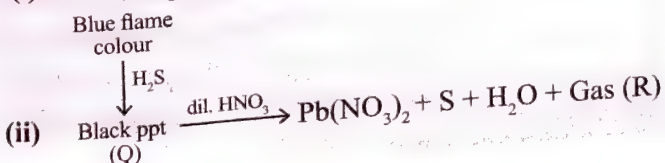
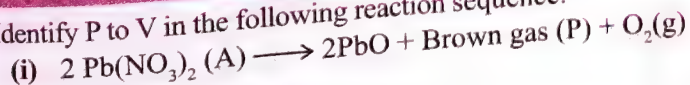
Thus (A) is ammonium dichromate.



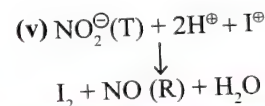
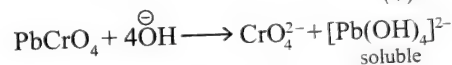
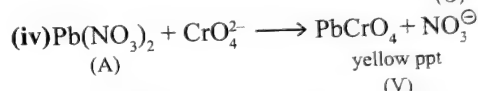
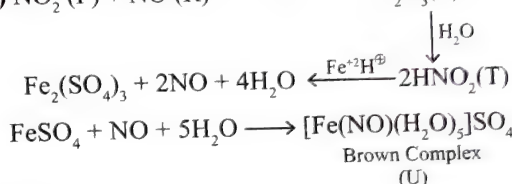
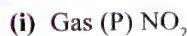
Hence (A) is (NH₄)₂Cr₂O₇, (B) is Cr₂O₃, (C) is N₂, (D) is Mg₃N₂ and (E) is NH₃.

EXAMPLE 2.8

Identify P to V in the following reaction sequence.



Sol.



EXAMPLE 2.9

In the following reactions, If total number of INCORRECT reactions are X, then the value of X is

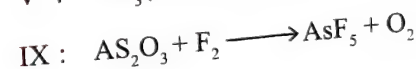
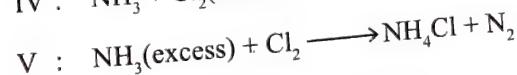
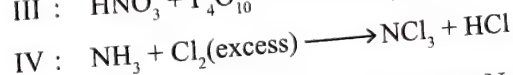
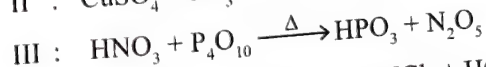
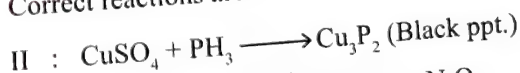
- $\text{CuSO}_4 + \text{NH}_3\text{(aq)} \longrightarrow$ complex is formed
- $\text{CuSO}_4 + \text{PH}_3 \longrightarrow$ complex is formed
- $\text{HNO}_3 + \text{P}_4\text{O}_{10} \xrightarrow{\Delta} \text{HPO}_3 + \text{N}_2\text{O}$
- $\text{NH}_3 + \text{Cl}_2\text{(excess)} \xrightarrow{\Delta} \text{NH}_4\text{Cl} + \text{N}_2$
- $\text{NH}_3\text{(excess)} + \text{Cl}_2 \xrightarrow{\Delta} \text{NCl}_3 + \text{HCl}$
- $\text{NH}_3 + \text{NaOCl} \longrightarrow \text{N}_2\text{H}_4 + \text{NaCl} + \text{H}_2\text{O}$
- $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{HNO}_3 \longrightarrow (\text{COOH})_2 + \text{NO}_2 + \text{H}_2\text{O}$
- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{Cr}_2\text{O}_3 + \text{N}_2 + 4\text{H}_2\text{O}$
- $\text{As}_2\text{O}_3 + \text{F}_2 \longrightarrow \text{AsF}_3 + \text{O}_2$

Sol.

Reaction I, VI, VII and VIII are correct.
 Reactions II, III, IV, V & IX are incorrect

$\therefore X = 5$

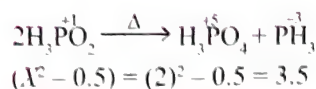
Correct reactions are:



EXAMPLE 2.10

If X is the number of moles required for the thermal decomposition of hypophosphorous acid, then the value of $(X^2 - 0.5)$ is

Sol. (3.5)

**EXAMPLE 2.11**

Consider the following compounds in their solid state and find the value of $(X + Y - Z/2)$

(i) PBr_5 (ii) PCl_5 (iii) N_2O_5

where X = Total number of cationic or anionic part is sp^3 hybridised.

Y = Total number of compounds having $109^\circ, 28^\circ$ bond angle either in cationic or anionic part.

Z = Total number of compounds having 90° bond angle either in cationic or anionic part.

Sol. (1.15)

Compound	Solid State	
(i) PBr_5	$[\text{PBr}_4]^+ \text{Br}^-$	
	sp^3	
	(109°, 28°)	
	$X = 1, Y = 1, Z = 0$	
(ii) PCl_5	$[\text{PCl}_4]^+$	$[\text{PCl}_6]^-$
	sp^3	sp^3d^2
	(109°, 28°)	(90°)
	$X = 1, Y = 1, Z = 1$	
(iii) N_2O_5	$[\text{NO}_2]^+$	$[\text{NO}_3]^-$
	sp	sp^2
	(180°)	(120°)

$$X = 0, Y = 0, Z = 0$$

$$\text{Total } X = 1 + 1 + 0 = 2$$

$$Y = 1 + 1 + 0 = 2$$

$$Z = 0 + 1 + 0 = 1$$

$$\therefore \left(\frac{X + Y - Z}{2} \right) = \left(\frac{2 + 2 - 1}{2} \right) = 1.5$$

EXAMPLE 2.12

Consider the following oxyanions:

(i) PO_4^{3-} (ii) HPO_3^{2-} (iii) H_2PO_2^- (iv) $\text{P}_2\text{O}_6^{4-}$

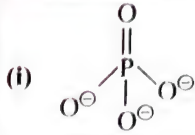
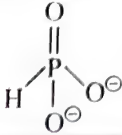
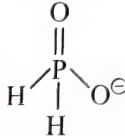
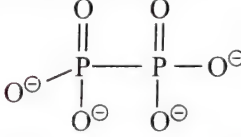
If X = Number of oxyanions having two equivalent P—O bonds per central atoms.

Y = Number of oxyanions having three equivalent P—O bonds per central atoms.

Z = Number of oxy anions having four equivalent P—O bonds per central atom.

Find the value of $2Z - \frac{(X + Y)}{2}$.

Sol.

Oxyanions	No. of equivalent bonds
(i)  Phosphate ion	$Z = 4$
(ii) HPO_3^{2-} Hydrogen phosphite ion 	$Y = 3$
Note : PO_3^{3-} does not exist, Since H_3PO_3 is dibasic.	
(iii) H_2PO_2^- (Dihydrogen phosphite ion) 	$X = 2$
Note : HPO_2^{2-} and PO_2^{3-} does not exist, since H_3PO_2 is monobasic.	
(iv) $\text{P}_2\text{O}_6^{4-}$ (Hypophosphate ion) 	$Y = 3$
$\therefore X = 2, Y = 3 + 3 = 6, Z = 4$	
$2Z - \frac{(X + Y)}{2} = 8 - 4 = 4$	

EXAMPLE 2.13

The following compounds on complete hydrolysis at room temperature gives the products.

(i) NO_2 and (ii) NCl_3

Identify the products which acts as:

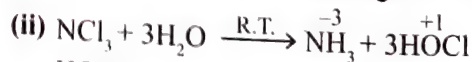
- Dibasic acid
- Flexidentate ligand
- Both oxidising and reducing agents.
- Monodentate ligands
- Non redox hydrolysis.

Sol.



b., d. NO_2^- and NO_3^- can act as flexidentate and monodentate ligands.

c. HNO_2 acts as both oxidising and reducing agent.



c. HOCl can act as both oxidising and reducing agent.

d. NH_3 acts as modentate ligand.

e. It is a non-redox hydrolysis.

Single Correct Answers Type

Physical Properties

- Select incorrect statement
 - (1) Single N—N bond is stronger than P—P bond.
 - (2) PH_3 can act as a ligand in the formation of coordination compound with transition element.
 - (3) NO_2 is paramagnetic in nature.
 - (4) Covalency of nitrogen in N_2O_5 is four.
- Reducing power of 15-group hydrides are in order:
 - (1) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
 - (2) $\text{BiH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$
 - (3) $\text{PH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
 - (4) $\text{BiH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{NH}_3 > \text{PH}_3$
- The boiling points of the hydrides of 15-group elements are in the order:
 - (1) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$
 - (2) $\text{NH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{PH}_3$
 - (3) $\text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
 - (4) $\text{AsH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{PH}_3$
- Elements of group-15 form compounds in +5 oxidation state. However, bismuth forms only one well characterized compound in +5 oxidation state. The compound is
 - (1) Bi_2O_5
 - (2) BiF_5
 - (3) BiCl_5
 - (4) Bi_2S_5
- In solid state PCl_5 is a
 - (1) Covalent solid
 - (2) octahedral structure
 - (3) Ionic solid $[\text{PCl}_6]^\oplus$ octahedral and $[\text{PCl}_4]^\ominus$ tetrahedral
 - (4) Ionic solid with $[\text{PCl}_4]^\oplus$ tetrahedral and $[\text{PCl}_6]^\ominus$ octahedral
- The boiling point of group 15 follows the order.
 - (1) $\text{N} < \text{P} < \text{Bi} < \text{Sb} < \text{As}$
 - (2) $\text{P} < \text{N} < \text{As} < \text{Bi} < \text{Sb}$
 - (3) $\text{N} < \text{Bi} < \text{P} < \text{Sb} < \text{As}$
 - (4) $\text{P} < \text{N} < \text{Bi} < \text{As} < \text{Sb}$
- Which of the following is the correct order of the thermal stability of hydrides
 - (1) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
 - (2) $\text{PH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
 - (3) $\text{BiH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
 - (4) $\text{NH}_3 > \text{BiH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
- The H—M—H bond angle of 15 group hydrides decrease from 107° to 90° from NH_3 to SbH_3 ; this is due to:
 - (1) increase in strength to bases with molecular weight
 - (2) use of pure *p*-orbital for M—H bonding in hydrides of higher molecular weight
 - (3) bond energies of M—H bonds increase
 - (4) bond pairs of electrons go closer to central atom.
- If *X* is number of P—O—P bonds in P_4O_{10} and *Y* is number of P—I bond in solid PI_3 . Then the value of (*X*—*Y*) is
 - (1) 1
 - (2) 2
 - (3) 3
 - (4) 4
- Boiling / melting points of the following hydrides follow in order
 - (1) $\text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 < \text{NH}_3$
 - (2) $\text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$
 - (3) $\text{SbH}_3 > \text{AsH}_3 < \text{PH}_3 < \text{NH}_3$
 - (4) $\text{SbH}_3 < \text{AsH}_3 < \text{PH}_3 < \text{NH}_3$
- Anomalous behaviour of nitrogen is due to
 - (1) Small size and high EN
 - (2) Non-ability of *d*-orbitals in valence shell
 - (3) Ease of multiple bond formation
 - (4) All
- The atomicity of phosphorus is *X* and the P—P—P bond angle is *Y*. What are *X* and *Y*?
 - (1) *X* = 4, *Y* = 90°
 - (2) *X* = 4, *Y* = 60°
 - (3) *X* = 3, *Y* = 120°
 - (4) *X* = 2, *Y* = 180°
- Nitrogen forms N_2 but phosphorus is converted into P_4 from P_2 . The reason for this is
 - (1) Triple bond is present between phosphorus atoms
 - (2) *pπ*—*pπ* bonding is weak
 - (3) *pπ*—*pπ* bonding is strong
 - (4) Multiple bond is formed easily
- The element which forms oxides in all the oxidation states from +1 to +5 is
 - (1) N
 - (2) P
 - (3) As
 - (4) Sb

Compounds of Nitrogen

- pπ*—*pπ* multiple bonding between nitrogen atoms is present in
 - (1) hyponitrous acid
 - (2) nitrous acid
 - (3) nitric acid
 - (4) in all of these
- The nitrogen that decomposes acetylene to cyanogens is
 - (1) Dinitrogen
 - (2) Active nitrogen
 - (3) Passive nitrogen
 - (4) Both (b) and (c)
- Which of the following statements about N_2O is false?
 - (1) A neutral oxide which does not form hyponitrous acid with water
 - (2) An oily liquid
 - (3) Used as propellant for whipped ice-cream
 - (4) Used as an anaesthetic
- Nitrogen dioxide :
 - (1) dissolves in water forming HNO_3
 - (2) does not dissolve in water
 - (3) dissolves in water to form HNO_2 and gives off O_2
 - (4) dissolves in water to form a mixture of nitrous and nitric acid

19. It is recommended that liquor ammonia bottle should be opened after cooling it in ice for sometime. This is because liquor ammonia:
- (1) brings tears in the eyes
 - (2) is a corrosive liquid
 - (3) is a mild explosive
 - (4) generates high vapour pressure
20. It is recommended that liquor ammonia bottle should be opened after cooling it in ice for sometime. This is because liquor ammonia:
- (I) The principal reducing product is NO gas
 - (II) Cu metal is oxidised to Cu^{2+} (aq.) ion which is blue in colour.
 - (III) NO is paramagnetic and has one unpaired electron in antibonding molecular orbital
 - (IV) No reacts with O_2 to produce NO_2 which is linear in shape
- Choose the correct statements:
- (1) I, II, III
 - (2) I, III
 - (3) II, IV
 - (4) All the above
21. A brown ring is formed in the ring test for NO_3^- ion. It is due to the formation of
- (1) $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$
 - (2) $\text{FeSO}_4 \cdot \text{NO}_2$
 - (3) $[\text{Fe}(\text{H}_2\text{O})_4(\text{NO})_2]^{2+}$
 - (4) $\text{FeSO}_4 \cdot \text{HNO}_3$
22. A black compound of manganese reacts with a halogen acid to give greenish yellow gas. When excess of this gas reacts with NH_3 an unstable trihalide is formed. In this process the oxidation state of nitrogen changes from....
- (1) -3 to +3
 - (2) -3 to 0
 - (3) -3 to +5
 - (4) 0 to -3
23. NO_2 is not obtained when following is heated:
- (1) $\text{Pb}(\text{NO}_3)_2$
 - (2) AgNO_3
 - (3) LiNO_3
 - (4) KNO_3
24. Laughing gas is prepared by heating
- (1) $\text{NH}_4\text{Cl} + \text{NaNO}_3$
 - (2) NH_4Cl
 - (3) $(\text{NH}_4)_2\text{SO}_4$
 - (4) NH_4NO_2
25. Which blue-liquid is obtained on reacting equimolar amounts of two gases at -30°C ?
- (1) N_2O
 - (2) N_2O_3
 - (3) N_2O_4
 - (4) N_2O_5
26. Which is the correct sequence in the following properties? For the correct order mark (T) and for the incorrect order mark (F):
- (a) Lewis acidity order : $\text{SiF}_4 < \text{SiCl}_4 < \text{SiBr}_4 < \text{SiI}_4$
 - (b) Melting point : $\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
 - (c) Boiling point : $\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
 - (d) Bond dipole order : $\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
- (1) FTFT
 - (2) TFFT
 - (3) FFTT
 - (4) FFTF
27. An orange solid (X) on heating gives a colourless gas (Y) and only a green residue (Z). Gas (Y) on treatment with Mg produces a white solid substance:
- (1) Mg_3N_2
 - (2) MgO
 - (3) Mg_2O_3
 - (4) MgCl_2
28. Calcium imide on hydrolysis will give gas (B) which on oxidation by bleaching powder given gas (C). Gas (C) on reaction with magnesium gives compound (D). (D) on hydrolysis gives again gas (B). (B), (C) and (D) are:
- (1) NH_3 , N_2 , Mg_3N_2
 - (2) N_2 , NH_3 , MgNH
 - (3) N_2 , N_2O_5 , $\text{Mg}(\text{NO}_3)_2$
 - (4) NH_3 , NO_2 , $\text{Mg}(\text{NO}_2)_2$
29. Among the following compounds, which on heating do not produce N_2 ?
- (1) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
 - (2) $\text{NH}_4\text{Cl} + \text{NaNO}_2$
 - (3) $\text{NH}_4\text{Cl} + \text{CaO}$
 - (4) $\text{Ba}(\text{N}_3)_2$
30. Nitrogen (I) oxide is produced by:
- (1) thermal decomposition of sodium nitrite at low temperature
 - (2) thermal decomposition of ammonium nitrite
 - (3) disproportionation of N_2O_4
 - (4) interaction of hydroxyl amine and nitrous acid
31. Match List-I with List-II and select the correct answer using the codes given below the lists:
- | List-I (Compounds) | | | | List-II (used in) |
|----------------------------------|-----|-----|-----|------------------------------------|
| (A) $\text{BaSO}_4 + \text{ZnS}$ | | | | (1) Explosive |
| (B) NI_3 | | | | (2) Oxidiser in rocket propellants |
| (C) N_2O_4 | | | | (3) Space capsule |
| (D) KO_2 | | | | (4) Pigment |
| (A) | (B) | (C) | (D) | |
| (1) 3 | 1 | 4 | 2 | |
| (2) 4 | 1 | 2 | 3 | |
| (3) 3 | 4 | 1 | 2 | |
| (4) 4 | 3 | 2 | 1 | |
32. Which of the following compound does not produce oxyacid of central atom on hydrolysis?
- (1) BF_3
 - (2) NCl_3
 - (3) SF_4
 - (4) PCl_3
33. The INCORRECT statement regarding 15th group hydrides (EH_3). [$E = \text{N, P, As, Sb, Bi}$]
- (1) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$: Thermal stability
 - (2) $\text{N}-\text{H} > \text{P}-\text{H} > \text{As}-\text{H} > \text{Sb}-\text{H} > \text{Bi}-\text{H}$: E-H bond dissociation enthalpy
 - (3) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$: Reducing character
 - (4) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$: Basicity
34. Which of the following oxyacid contains both P-H and P-P bond simultaneously?
- (1) $\text{H}_4\text{P}_2\text{O}_5$
 - (b) $\text{H}_4\text{P}_2\text{O}_7$
 - (3) $\text{H}_4\text{P}_2\text{O}_6$
 - (4) None

35. Among the following statement which one is true?
 (1) NH_3 is less soluble than PH_3 in water
 (2) NH_3 is stronger base and stronger reducing agent than PH_3
 (3) NH_3 has higher boiling point than PH_3 and has lower melting point than PH_3
 (4) PH_3 is stronger reducing agent than NH_3 and it has lower critical temperature than NH_3
36. Which of the following statements regarding N_2O_4 is NOT CORRECT?
 (1) It is a planar molecule
 (2) It is used as non-aqueous solvent
 (3) It involves N—N bond which is larger than the N—N bond in hydrazine
 (4) Ammonium nitrate in N_2O_4 acts as a base
37. Which of the following on heating produces NO_2 ?
 (1) NaNO_3 (2) AgNO_3
 (3) NH_4NO_3 (4) NH_4NO_2
38. Which of the following equation is wrong ?
 (1) $\text{P}_4 + 20\text{HNO}_3 \longrightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}$
 (2) $\text{I}_2 + 10\text{HNO}_3 \longrightarrow 2\text{HIO}_4 + 10\text{NO}_2 + 4\text{H}_2\text{O}$
 (3) $\text{S} + 6\text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + 6\text{NO}_2 + 2\text{H}_2\text{O}$
 (4) None of the above
39. Nitrogen gas is liberated by thermal decomposition of:
 (1) NH_4NO_2 (2) NaN_3
 (3) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (4) All
40. Two oxides of nitrogen, NO and NO_2 are allowed to react together at 243°K and form a coloured compound of nitrogen (X). When compound (X) reacts with water to yield another compound of nitrogen (Y). The shape of the anion of (Y) molecule is:
 (1) triangular planar (2) triangular pyramidal
 (3) tetrahedron (4) square planar
41. Consider the following sequence of reaction.

$$\text{Na} + \text{NH}_3(\text{g}) \longrightarrow [\text{X}] \xrightarrow{\text{N}_2\text{O}} [\text{Y}] \xrightarrow{\text{Heat}} [\text{Z}]$$
 Gas Pure
 Identify $[\text{Z}]$ gas:
 (1) N_2 (2) NH_3
 (3) O_2 (4) H_2
42. $\text{NH}_3 + \text{O}_2 \xrightarrow[\Delta]{\text{Pt}} \text{A} + \text{H}_2\text{O}$;
 $\text{A} + \text{O}_2 \longrightarrow \text{B}$;
 $\text{B} + \text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{C}$;
 A , B and C are:
 (1) N_2O , NO_2 and HNO_3 (2) NO , NO_2 and HNO_3
 (3) NO_2 , NO and HNO_3 (4) N_2O , NO and HNO_3
43. The mixed anhydride of nitrous and nitric acid is
 (1) N_2O (2) NO_2
 (3) NO (4) N_2O_5
44. Copper reacts with dil. HNO_3 to form a nitrate and
 (1) NO_2 (2) NO
 (3) N_2O_3 (4) N_2O_5
45. Nitrogen sesquioxide is
 (1) N_2O_3 (2) N_2O_4
 (3) N_2O_5 (4) N_2O
46. When silver nitrate is heated, the products are
 (1) Oxygen and metal nitrite
 (2) Nitrogen dioxide, O_2 and metallic oxide
 (3) Nitrogen dioxide, O_2 and metal
 (4) Nitrogen dioxide and metal oxide
47. NO is purified by
 (1) Absorption in $(\text{NH}_4)_2\text{SO}_4$ solution
 (2) Passing into conc. H_2SO_4
 (3) Absorbing in FeSO_4 solution
 (4) Electrolysis method
48. Which of the following combines with Fe^{2+} ions to form brown complex?
 (1) NO (2) N_2O
 (3) N_2O_3 (4) N_2O_5
49. Nitrogen reacts with calcium and carbon or when N_2 gas is passed over heated calcium carbide (at 1070 K) it gives _____ which is an important fertiliser marketed under the name Nitrolim
 (1) Calcium nitrate (2) Calcium cyanide
 (3) Calcium cyanamide (4) Calcium nitride
50. Ordinary strong solution of HCl , HNO_3 and H_2SO_4 contains roughly
 (1) 1/5, 2/3 and 3/3 fractions of pure acid and water respectively
 (2) 2/3, 1/5 and 3/3 fractions of pure acid and water respectively
 (3) 2/3, 3/3 and 1/5 fractions of pure acid and water respectively
 (4) None
51. Dilute HNO_3 cannot be concentrated beyond 68% by boiling because
 (1) On boiling HNO_3 is decomposed
 (2) On boiling HNO_3 produces a large amount of heat which is uncontrollable
 (3) It forms a constant boiling mixture with H_2O boiling at 394 K
 (4) It can be concentrated beyond 68% by steam distillation
52. Fuming HNO_3 (containing 98% of HNO_3) is obtained
 (1) By distilling 68% HNO_3 with conc. H_2SO_4
 (2) By distilling 68% HNO_3 under reduced pressure
 (3) By steam distillation of 68% HNO_3
 (4) By distillation 68% HNO_3 with P_4O_{10}
53. Nitrolim is
 (1) CaCN_2 (2) $\text{CaCN}_2 + \text{C}$
 (3) CaC_2 (4) $\text{CaCN}_2 + \text{CaC}_2$

54. Nitrochalk is
 (1) CAN (2) CaNCN
 (3) $(\text{NH}_4)_2\text{SO}_4$ (4) $\text{Ca}(\text{NO}_3)_2 \cdot \text{CaO}$
55. Which of the following acid posses oxidising, reducing and complex forming properties?
 (1) HNO_3 (2) HNO_2
 (3) H_2SO_4 (4) HCl
56. Acidic hydride of nitrogen is
 (1) NH_3 (2) N_3H
 (3) N_2H_4 (4) N_2H_2
57. Which one of the following pairs is obtained on heating ammonium dichromate?
 (1) N_2 and H_2O (2) N_2O and H_2O
 (3) NO and H_2O (4) NO and NO_2
58. In salt which on heating gives a mixture of two gases is
 (1) NaNO_3 (2) KNO_3
 (3) $\text{Pb}(\text{NO}_3)_2$ (4) NH_4NO_3
59. When ammonia is heated with CO_2 under pressure, the product is
 (1) $(\text{NH}_4)_2\text{CO}_3$ (2) NH_2CONH_2
 (3) $\text{NH}_2\text{COONH}_4$ (4) NH_4HCO_3
60. When treated with nitric acid which of the following liberates hydrogen?
 (1) Zinc (2) Copper
 (3) Magnesium (4) Mercury
61. The reaction between NH_2^\ominus and N_2O gives
 (1) NO (2) N_2O_5
 (3) NH_2NH_2 (4) N_3^\ominus
62. Hydrolysis of NCl_3 gives NH_3 and X. Which of the following is X?
 (1) HClO_4 (2) HClO_3
 (3) HOCl (4) HClO_2
63. Chlorine reacts with excess of ammonia to form
 (1) NH_4Cl (2) $\text{N}_2 + \text{HCl}$
 (3) $\text{N}_2 + \text{NH}_4\text{Cl}$ (4) $\text{N}_2 + \text{NCl}_3$
64. In NO_3^\ominus ion, the number of bond pair and lone pair of electrons on nitrogen atoms are
 (1) 2, 2 (2) 3, 1
 (3) 1, 3 (4) 4, 0
65. A pale blue liquid which is obtained by reacting equimolar mixture of two gases at -30°C is
 (1) N_2O_3 (2) N_2O
 (3) N_2O_4 (4) N_2O_5
66. The INCORRECT order is:
 (1) Thermal stability : $\text{HF} > \text{HCl} > \text{HBr}$
 (2) Lewis basic character: $\text{PF}_3 < \text{PCl}_3 < \text{PBr}_3$
 (3) % *p*-character : $\text{NO}_2^+ > \text{NO}_3^- > \text{NH}_4^+$
 (4) Bond angle : $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3$

Compounds of Phosphorous

67. Calculate $x + y + z$ for H_3PO_3 acid, where x is number of lone pairs, y is number of σ -bonds and z is number of π -bonds:
 (1) 5 (2) 14
 (3) 13 (4) 12
68. A non-metal M forms MCl_3 , M_2O_5 and Mg_3M_2 but does not form MI_5 . Then incorrect statement regarding non-metal M is:
 (1) M can form multiple bond
 (2) M is of second period element
 (3) Atomicity of non-metal is 4
 (4) The range of oxidation number for M is +5 to -3
69. The formation of PH_4^\oplus is difficult compared to NH_4^\oplus because:
 (1) lone pair of phosphorus is optically inert
 (2) lone pair of phosphorus resides in almost pure *p*-orbital
 (3) lone pair of phosphorus resides at sp^3 orbital
 (4) lone pair of phosphorus resides in almost pure *s*-orbital
70. In a cyclotrimetaphosphoric acid molecule, how many single and double bonds are present?
 (1) 3 double bonds; 9 single bonds
 (2) 6 double bonds; 6 single bonds
 (3) 3 double bonds; 12 single bonds
 (4) Zero double bonds; 12 single bonds
71. Amongst the following compounds
 (I) $\text{H}_5\text{P}_3\text{O}_{10}$ (II) $\text{H}_6\text{P}_4\text{O}_{13}$
 (III) $\text{H}_5\text{P}_5\text{O}_{15}$ (IV) $\text{H}_7\text{P}_5\text{O}_{16}$
 non-cyclic phosphates are:
 (1) I, III (2) I, II, III
 (3) I, II, IV (4) I, II, III, IV
72. Strong reducing behaviour of H_3PO_2 is due to
 (1) Low oxidation state of phosphorus
 (2) Presence of two $-\text{OH}$ Group and one $\text{P}-\text{H}$ bonds
 (3) Presence of one $-\text{OH}$ group and two $\text{P}-\text{H}$ bonds
 (4) High electron gain enthalpy of phosphorus
73. The cyclotrimetaphosphoric acid is:
 (1) $(\text{HPO}_3)_3$ and contains 9 σ -bonds
 (2) $\text{H}_3\text{P}_3\text{O}_6$ and contains 12 σ -bonds
 (3) $(\text{HPO}_3)_3$ and contains 15 σ -bonds
 (4) $\text{H}_3\text{P}_3\text{O}_6$ and contains 18 σ -bonds
74. Which of the following acids forms three series of salts?
 (1) H_3PO_2 (2) H_3PO_3
 (3) H_3PO_4 (4) H_3PO_3
75. $\text{A} + \text{H}_2\text{O} \longrightarrow \text{B} + \text{HCl}$
 $\text{B} + \text{H}_2\text{O} \longrightarrow \text{C} + \text{HCl}$
 Compound (A), (B) and (C) will be respectively:
 (1) PCl_5 , POCl_3 , H_3PO_3 (2) PCl_5 , POCl_3 , H_3PO_4
 (3) SOCl_2 , POCl_3 , H_3PO_3 (4) PCl_3 , POCl_3 , H_3PO_4

76. The product formed in the reaction of SOCl_2 with white phosphorus is:

- I. PCl_3 II. SO_2 III. S_2Cl_2 IV. POCl_3

- (1) I, II, III (2) II, III, IV
(3) I, II (4) III, IV

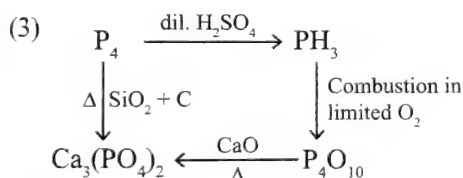
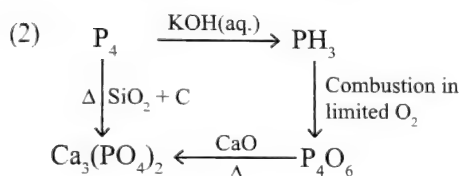
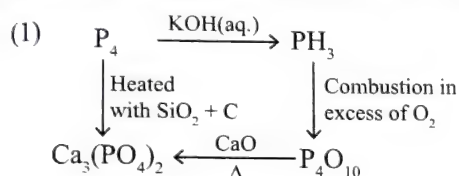
77. In which of the following compounds hydrolysis takes place through $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ mechanism respectively?

- (1) NF_3 , NCl_3 (2) P_4O_{10} , SiCl_4
(3) SF_4 , TeF_6 (4) SiCl_4 , SiF_4

78. Incorrect statement about PH_3 is:

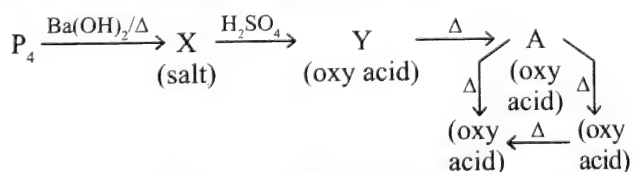
- (1) It is produced by hydrolysis of Ca_3P_2
(2) It gives black ppt. (Cu_3P_2) with CuSO_4 solution
(3) Spontaneously burns in presence of P_2H_4
(4) It does not react with B_3H_6

79. Which of the following reacting sequence is correct regarding conversion of phosphorus compounds?



(4) None of these.

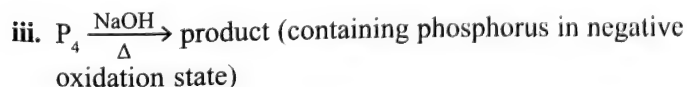
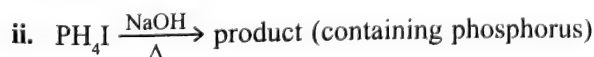
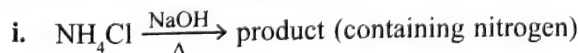
80. Consider the following sequence of reaction:



In the above sequence of reactions Y and A are respectively:

- (1) H_3PO_2 and H_3PO_4 (2) H_3PO_4 and $\text{H}_3\text{P}_2\text{O}_7$
(3) H_3PO_4 and HPO_3 (4) H_3PO_3 and H_3PO_4

81. Consider the following reactions:



The order of change in bond angle (for reactant \rightarrow specified product) is:

- (1) (i) > (ii) > (iii) (2) (ii) > (iii) > (i)
(3) (iii) > (ii) > (i) (4) (ii) > (i) > (iii)

82. In which of the following acids, P—P bonds is present?

- (1) Tetra poly phosphoric acid ($\text{H}_6\text{P}_4\text{O}_{13}$)
(2) Pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$)
(3) Hypophosphoric acid ($\text{H}_4\text{P}_2\text{O}_6$)
(4) Polymetaphosphoric acid (HPO_3)_n

83. Of the following the most acidic is

- (1) H_3PO_4 (2) H_3AsO_4
(3) H_3SbO_4 (4) H_3BiO_4

84. Which of the following form maximum P—H bonds.

- (1) H_3PO_2 (2) H_3PO_4
(3) H_3PO_3 (4) $\text{H}_4\text{P}_2\text{O}_7$

85. PCl_5 in solid state exists as

- (1) PCl_5 (2) PCl_4^+
(3) PCl_6^- (4) $\text{PCl}_4^+ \text{PCl}_6^-$

86. Graham's salt used for softening of water and with other alkalis used for cleaning sinks, drains and floors is

- (1) $(\text{NaPO}_3)_n$ (2) $(\text{KPO}_3)_n$
(3) Na_3PO_4 (4) K_3PO_4

87. The structure of phosphide ion is similar to that of

- (1) Nitride ion (2) Chloride ion
(3) Fluoride ion (4) Sodium ion

88. Calcium phosphide is used in smoke screen because it

- (1) Burns to form soot
(2) Gives phosphine which catches fire to give needed smoke
(3) Immediately catches fire in air
(4) Is a gas which brings tears in the eyes

89. Holme's signals produce burning gases which serve as a signal to the approaching ships contains

- (1) A mixture of Ca_3P_2 and CaC_2
(2) A mixture of Ca_3P_2 and KOH
(3) A mixture of CaC_2 and KOH
(4) A mixture of Ca_3P_2 , CaC_2 and KOH

90. PCl_3 , P_4O_6 and P_4O_{10} , PCl_5 on hydrolysis gives respectively

- (1) H_3PO_3 and H_3PO_4 (2) H_3PO_4 and H_3PO_3
(3) $(\text{HPO}_3)_n$ and $\text{H}_4\text{P}_2\text{O}_7$ (4) $\text{H}_4\text{P}_2\text{O}_7$ and $(\text{HPO}_3)_n$

91. The number of P—O—P and P—OH bonds present respectively in pyrophosphoric acid molecule are

- (1) 2, 3 (2) 1, 8
(3) 1, 4 (4) 1, 2

92. When phosphine is bubbled through a solution of nitrate _____ is precipitated.

- (1) Silver (2) Silver phosphide
(3) Silver oxide (4) None of these

93. When orthophosphoric acid is heated at 240°C , the main product formed is

- (1) H_3PO_3 (2) H_3PO_2
(3) HPO_3 (4) $\text{H}_4\text{P}_2\text{O}_7$

94. White phosphorus reacts with caustic soda. The products are PH_3 and NaH_2PO_2 . This reaction is an example of
 (1) Oxidation (2) Reduction
 (3) Neutralisation (4) Disproportionation
95. The number of P—O—P bridges in the structure of P_4O_{10} and P_4O_6 are respectively
 (1) 5, 5 (2) 5, 6
 (3) 6, 6 (4) 6, 5
96. Cl—P—Cl bond angles in PCl_5 molecule are
 (1) 120° and 90° (2) 60° and 90°
 (3) 60° and 120° (4) 120° and 30°
97. Scheel's green, formerly used as a green pigment for colouring wall paper is
 (1) Sodium arsenite (Na_3AsO_3)
 (2) Cupric arsenite (CuHAsO_3)
 (3) Silver arsenite (Ag_3AsO_3)
 (4) None
98. Paris green was used as a pigment due to unique light green colour but now-a-days it is used as an insecticide. It is prepared by boiling verdigris (basic acetate of copper), arsenious oxide and acetic acid together. It is
 (1) $(\text{CH}_3\text{COO})_2\text{Cu} \cdot 3\text{Cu}(\text{AsO}_2)_2$
 (2) Cupric acetoarsenite
 (3) $\text{Cu}_4(\text{CH}_3\text{COO})_2(\text{AsO}_2)_2$
 (4) All
99. Tartar emetic (potassium antimony tartrate) is used as an emetic in small doses while larger doses are poisonous. It is used for the treatment of Kala-azar and such other tropical diseases. It is formed when antimony trioxide (Sb_2O_3) is treated with potassium hydrogen tartrate. It is
- | | |
|--------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|
| (1) $\begin{array}{c} \text{CH(OH) COO (SbO)} \\ \\ \text{CH(OH) COOK} \end{array}$ | (2) $\begin{array}{c} \text{CH(OH) COO (Sb)} \\ \\ \text{CH(OH) COOK} \end{array}$ |
| (3) $\begin{array}{c} \text{CH(OH) COO (Sb}_2\text{O}_3) \\ \\ \text{CH(OH) COOK} \end{array}$ | (4) $\begin{array}{c} \text{CH(OH) COO (SbO}_3) \\ \\ \text{CH(OH) COOK} \end{array}$ |
100. Which one of the following halide does not hydrolyse?
 (1) SbCl_3 (2) AsCl_3
 (3) PCl_3 (4) NF_3
101. Wittig reagent is used for the synthesis of alkenes from ketone in organic chemistry. The Wittig reagent is
 (1) $(\text{Ph}_3\text{P})=\text{CH}_2$ Triphenyl phosphine methylene
 (2) $(\text{Ph}_3\text{P})=\text{O}$ Triphenyl phosphine oxide
 (3) $(\text{Ph}_3\text{P})\text{CH}_3\text{Br}$
 (4) Ph_3P
102. Following tests are shown by
 i. Decolourisation of acidified soln. of KMnO_4
 ii. Liberation of I_2 from an acidified soln. of KI
 iii. On treatment with dil HCl , brown fumes of NO_2 which turns FeSO_4 soln. black
- (1) Nitrites (2) Nitrates
 (3) Both (a) and (b) (4) Neither (a) nor (b)
103. PCl_5 exist but NCl_5 does not because
 (1) NCl_5 is unstable
 (2) Nitrogen has no vacant orbitals
 (3) Nitrogen atom is much smaller
 (4) Nitrogen is highly inert
104. PCl_5 and PH_3 exist but PH_5 does not because
 (1) PH_5 is unstable
 (2) Phosphorous has no vacant orbitals
 (3) Phosphorous exists as P_4
 (4) EN of hydrogen is less as compared to chlorine to excite electron from p orbital to d orbital for bond formation
105. N_2 forms NCl_3 whereas P can form both PCl_3 and PCl_5 . Why?
 (1) P has d -orbitals which can be used for bonding but N does not have
 (2) N atom is larger than P in size
 (3) P is more reactive towards Cl than N
 (4) None of the above
106. The following are some statements related to group 15 hydrides
 i. Reducing property increases from NH_3 to BiH_3
 ii. Tendency to donate lone pair decreases from NH_3 to BiH_3
 iii. Thermal stability of hydrides decreases from NH_3 to BiH_3
 iv. Bond angle decreases from NH_3 to BiH_3
 The correct statements are:
 (1) (i), (ii), (iii) and (iv) (2) (i), (iii) and (iv)
 (3) (i), (ii) and (iv) (4) (i) and (iv)
107. Phosphine, acetylene and ammonia can be formed by treating water with
 (1) Mg_3P_2 , Al_4C_3 , Li_3N (2) Ca_3P_2 , CaC_2 , Mg_3N_2
 (3) Ca_3P_2 , CaC_2 , CaCN_2 (4) Ca_3P_2 , Mg_2C , NH_4NO_3
108. The CN^\ominus ion and N_2 are isoelectronic. But in contrast to CN^\ominus , N_2 is chemically inert because of
 (1) Low bond energy
 (2) Absence of bond polarity
 (3) Unsymmetrical electron distribution
 (4) Presence of more number of electrons in bonding orbitals
109. White phosphorus on reaction with lime water gives calcium salt of an acid (A) along with a gas (X). Which of the following is correct?
 (1) (A) on heating gives (X) and O_2
 (2) The bond angle in (X) is less than that in case of ammonia
 (3) (A) is a dibasic acid
 (4) (X) is more basic than ammonia

110. One mole of H_3PO_3 on reaction with excess of NaOH gives:
 (1) One mole of Na_2HPO_3 (2) Two moles of $\text{Na}_2\text{H}_2\text{PO}_3$
 (3) Two moles of Na_2HPO_3 (4) One mole of Na_3PO_3
111. If O_2 is removed from the formula of anhydride of HNO_2 , then the formula of the resulting compound satisfies which of the following properties?
 (1) It produces tears in eyes
 (2) It supports combustion
 (3) It is paramagnetic
 (4) It cannot react with red hot copper
112. Which of the following statements is correct?
 (1) N_2O is a laughing gas and is angular in shape
 (2) NO_2 is a sweet smelling and is angular in shape
 (3) NO is a colourless gas and acidic in nature
 (4) NO_2 on reaction with NaOH gives a mixture of two Salts
113. The compound is covalent in gaseous state but ionic in solid state is
 (1) PCl_5 (2) PCl_3
 (3) CCl_4 (4) NH_3
114. The equivalent mass of phosphoric acid (H_3PO_4) in reaction, $\text{NaOH} + \text{H}_3\text{PO}_4 \longrightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$, is
 (1) 29 (2) 49
 (3) 59 (4) 98
115. The oxyacid of phosphorus in which phosphorus has lowest oxidation state is
 (1) Hypophosphorus acid (2) Orthophosphoric acid
 (3) Pyrophosphoric acid (4) Metaphosphoric acid
116. Which is/are correct statements about P_4O_6 and P_4O_{10} :
 (1) In P_4O_6 each P is joined to three O and in P_4O_{10} each P is linked to four O atoms.
 (2) Both (a) and (b) form oxoacids H_3PO_3 and H_3PO_4 respectively
 (3) Both (a) and (b)
 (4) None
117. Blue liquid which is formed at -30°C by mixing of two gases is
 (1) N_2O (2) N_2O_4
 (3) N_2O_3 (4) N_2O_5
3. Which is true about N_2O_5 ?
 (1) It is anhydride of HNO_3
 (2) In solid state it exists as $\text{NO}_2^+ \text{NO}_3^-$
 (3) It is structurally similar to P_2O_5
 (4) It can be prepared by heating HNO_3 over P_2O_5
4. Orthophosphoric acid $\xrightarrow[220^\circ\text{C}]{\text{gentle heat}}$ P
 What is/are correct about P?
 (1) It is a tetrabasic acid
 (2) It contains one $\text{P} - \text{O} - \text{P}$ bond
 (3) It is a dibasic acid
 (4) On hydrolysis it produces metaphosphoric acid
5. At high temperatures, nitrogen directly does not combine with:
 (1) Zn (2) Mg
 (3) Al (4) Fe
6. Which product(s) is not obtained in the following reaction?
 $\text{P} + \text{OH} \longrightarrow \text{Product(s)}$
 (1) PH_3 (2) PO_4^{2-}
 (3) H_2PO_2^- (4) PO_2^-
7. Phosphine is not obtained by the reaction when:
 (1) White phosphorus is heated with NaOH
 (2) Ca_3P_2 reacts with water
 (3) red phosphorus is heated with NaOH
 (4) phosphorus is heated in current of hydrogen
8. Which of the following statements is/are incorrect?
 (1) NO_2 is a diamagnetic substance
 (2) Solid is brown in colour
 (3) NO_2 dimerizes to N_2O_4
 (4) NO_2 is a mixed anhydride
9. Which of the following statements are true about P_4O_6 and P_4O_{10} ?
 (1) Both these oxides have a closed cage like structure
 (2) Each oxide requires 6 water molecules for complete hydrolysis to form their respective oxoacids
 (3) Both these oxides contain 12 equivalent $\text{P} - \text{O}$ bonds
 (4) P_4O_6 and P_4O_{10} both contains $\text{p}\pi - \text{d}\pi$ bonds
10. Which of the following, when dissolved in water, will liberate ammonia?
 (1) NaNO_3 (2) NaNO_2
 (3) NaNH_2 (4) Na_3N_2
11. Which of the following is not true for allotropes or phosphorus?
 (1) Yellow phosphorus is soluble in CS_2 while red phosphorus is not
 (2) $\text{P} - \text{P} - \text{P}$ bond angle is 60° in red phosphorus
 (3) On heating in air, white phosphorus changes to red
 (4) White phosphorus slowly changes to red phosphorus at ordinary temperatures

Multiple Correct Answers Type

Physical Properties

1. Which of the following act as an oxidising as well as a reducing agent?
 (1) HNO_2 (2) H_2O_2
 (3) H_2S (4) SO_2
2. White phosphorus cannot be separated from red phosphorus by:
 (1) sublimation (2) dissolving in CS_2
 (3) distillation (4) heating and alkali solution

12. PH_3 can be obtained by:

- (1) heating hypophosphorus acid
- (2) heating orthophosphorus acid
- (3) reaction of P_4 with hot conc. NaOH
- (4) hydrolysis of calcium phosphide

13. Select the correct trends.

- (1) $\text{N} < \text{P} < \text{Bi} < \text{Sb} < \text{As}$ (Melting point)
- (2) $\text{N} > \text{P} > \text{As} > \text{Sb} > \text{Bi}$ (Ionisation energy)
- (3) $\text{N} > \text{P} > \text{As} > \text{Sb} > \text{Bi}$ (Electronegativity)
- (4) $\text{P} < \text{N} < \text{As} < \text{Bi} < \text{Sb}$ (Melting point)

14. Which of the following statements are INCORRECT?

- (1) The number of $\text{P} - \text{O} - \text{P}$ bond in P_4O_6 , P_4O_8 and P_4O_{10} are equal in number.
- (2) P_4O_8 and P_4O_{10} have 5 $\text{P} - \text{O} - \text{P}$ bonds
- (3) P_4O_{10} has 4 ' $-\text{P}=\text{O}$ '
- (4) P_4O_6 and P_4O_8 have zero and two $-\text{P}=\text{O}$ bonds respectively.

15. Which of the following orders are correct according to indicated property

- (1) $\text{N}_2\text{O} < \text{NO} < \text{N}_2\text{O}_3 < \text{N}_2\text{O}_4 < \text{N}_2\text{O}_5$ (strength of oxides of nitrogen)
- (2) P_4O_6 and $\text{N}_2\text{O}_3 < \text{As}_4\text{O}_6 > \text{Sb}_4\text{O}_6$ (acidic strength of trioxides)
- (3) $\text{N}_2\text{O}_5 > \text{P}_4\text{O}_{10} > \text{As}_4\text{O}_{10} > \text{Sb}_4\text{O}_6$ (acidic strength of pentoxides)
- (4) $\text{PI}_3 < \text{PBr}_3 > \text{PCl}_3 > \text{PF}_3$ (Bond angle)

16. Choose the correct statements

- (1) $\text{NF}_3 < \text{NCl}_3 < \text{NBr}_3 < \text{NI}_3$ (Lewis base strength)
- (2) In hydrolysis of SbCl_3 , the addition of excess of HCl suppresses the hydrolysis by shifting the equilibrium to the left
- (3) NF_3 does not undergo hydrolysis
- (4) Thermal stability of $\text{PCl}_3 > \text{PCl}_5$

17. Which of the following statements are incorrect?

- (1) All the three $\text{N} - \text{O}$ bond length in HNO_3 are equal
- (2) All $\text{P} - \text{C}$ bond length in PCl_5 molecule in gaseous state are equal
- (3) P_4 molecule in white phosphorus have angular strain therefore white phosphorus is very reactive
- (4) PCl_5 is ionic in solid state in which cation is octahedral and anion tetrahedral

Compounds of Nitrogen

18. Which of the following compounds is NOT obtained when HNO_3 reacts with P_4O_{10} .

- (1) N_2O_5
- (2) NO_2
- (3) NO
- (4) HPO_3

19. Which of the following compound(s) are explosive(s)?

- (1) NCl_3
- (2) NI_3
- (3) NBr_3
- (4) NF_3

20. The following side reaction in the production of N_2H_4

$$\text{N}_2\text{H}_4 + 2\text{NH}_2\text{Cl} \longrightarrow \text{N}_2 + 2\text{NH}_4\text{Cl}$$

- (1) is catalysed by traces of heavy metals as Cu^{2+}
- (2) is suppressed by addition of gelatin or glue
- (3) is made reversible by removing N_2
- (4) is made reversible by adding NaOH

21. The nitrogen oxide(s) that contain(s) $\text{N}-\text{N}$ bond(s) is (are)

- (1) N_2O
- (2) N_2O_3
- (3) N_2O_4
- (4) N_2O_5

22. N_2H_4 reduces IO_3^-/H^+

- (1) to I^\oplus
- (2) with I_2 as an intermediate indicated by violet colour in CCl_4 layer
- (3) indicated by blue colour with starch
- (4) to I^\ominus

23. Ammonia reacts with Nessler's reagents to give a brown ppt. due to formation of

- (1) $\text{H}_2\text{N}-\text{Hg}-\text{O}-\text{HgI}$
- (2) IO_3^\ominus
- (3) Iodide of Millon's base
- (4) K_2HgI_4

24. Which of the following are used as fertilizers?

- (1) $\text{Ca}_3(\text{PO}_4)_2$
- (2) $\text{Ca}(\text{H}_2\text{PO}_4)_2$
- (3) CaNCN
- (4) CaC_2

25. Photochemical decomposition of HNO_3 produces:

- (1) N_2
- (2) N_2O
- (3) NO_2
- (4) O_2

26. Which of the following statement(s) regarding nitrogen sesquioxide (N_2O_3) is/are correct?

- (1) Nitrogen sesquioxide is stable only in the liquid state. It dissociates in the vapour state
- (2) Nitrogen sesquioxide is a neutral oxide
- (3) Nitrogen sesquioxide contains a weak $\text{N} - \text{N}$ bond
- (4) Nitrogen sesquioxide exists in two different forms

27. Select the correct reaction(s)

- (1) $\text{NH}_4\text{NO}_3 \xrightarrow{250^\circ\text{C}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$
- (2) $\text{NH}_2\text{OH} + \text{HNO}_2 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$
- (3) $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}$
- (4) $\text{As}_2\text{O}_3 + \text{HNO}_3(\text{dil}) \longrightarrow \text{N}_2\text{O}_3 + 2\text{H}_3\text{AsO}_4$

28. The metals which produce hydrogen only with very dilute nitric acid are

- (1) Zn
- (2) Cu
- (3) Mg
- (4) Mn

29. The nitrogen oxide(s) that contain(s) $\text{N} - \text{N}$ bond(s) is (are)

- (1) N_2O
- (2) N_2O_3
- (3) N_2O_4
- (4) N_2O_5

30. A solution of colourless salt on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime upon addition of Zn dust to the same solution. The gas evolution restarts. The colourless salt(s) is (are)

- (1) NH_4NO_3 (2) NH_4NO_2
 (3) NH_4Cl (4) $(\text{NH}_4)_2\text{SO}_4$

Compounds of Phosphorous

31. Which of the following are similarities between $\text{H}_4\text{P}_4\text{O}_{12}$ and $\text{H}_4\text{P}_2\text{O}_7$?
 (1) Structure
 (2) Total number of atoms directly bonded to each phosphorous atom
 (3) Type of linkage (X—O—X/X—X)
 (4) Number of P—O—P linkage

32. PCl_5 is formed when:

- (1) white phosphorus reacts with limited dry chlorine
 (2) white phosphorous reacts with excess of dry chlorine
 (3) white phosphorus reacts with excess of SO_2Cl_2
 (4) white phosphorus reacts with excess of SO_2Cl_2

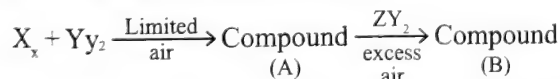
33. Which of the following is incorrect for P_4 molecule of white phosphorus?

- (1) It has 6 lone pairs of electron
 (2) It has 6 P—P single bonds
 (3) It has 3 P—P single bonds
 (4) It has 4 lone pairs of electrons

34. Which of the following statements are incorrect?

- (1) In phosphorous acids, formal oxidation state of P is +1 and +3
 (2) In phosphoric acids, formal oxidation state of P is +5.
 (3) The oxoacids in +3 oxidation state undergo disproportionation reaction to give compounds in lower and higher oxidation states.
 (4) H_3PO_3 is stronger reducing agent than H_3PO_2 .

35. Consider the following reactions:



(Atomic number of element X and Y are 15 and 8)

Select the correct statements :

- (1) (Y—X—Y) bond angle in B > (Y—X—Y) bond angle in A.
 (2) (X—Y) bond length in B < (X—Y) bond length in A.
 (3) Compound A is P_2O_5 and compound B is P_4O_{10}
 (4) Value of $X + Y + Z = 9$

36. Consider the following reactions:

- (i) Hydrolysis of one mole of calcium phosphide
 (ii) Reaction of KOH with 1 mole of white P_4 .

If X is the number of moles of H_2O in reaction (i) and Y is the number of P—H bonds in the products of reaction (ii).

Select the correct statements

- (1) PH_3 is formed in both reactions
 (2) $\text{H}_2\text{PO}_2^\ominus$ is formed in reaction (i)
 (3) The value of Y is 5.
 (4) The value of $X - Y = 1$.

37. What is/are not true about phosphine (PH_3)?

- (1) It turns red litmus blue.
 (2) It reacts with HCl(aq.) to give PH_4Cl
 (3) Phosphonium compounds are obtained when anhydrous phosphine reacts with anhydrous halogen acids.
 (4) It is prepared by hydrolysis of metal phosphides with acids.

38. Which of the following reactions can evolve phosphine?

- (1) $\text{White P} + \text{Ca(OH)}_2 \longrightarrow$
 (2) $\text{AlP} + \text{H}_2\text{O} \longrightarrow$
 (3) $\text{H}_3\text{PO}_4 \xrightarrow{\text{Heat}}$
 (4) $\text{PH}_4\text{I} + \text{NaOH} \longrightarrow$

Linked Comprehension Type

Paragraph 1

NH_3 has got pyramidal structure. By replacement of H atoms it forms $(\text{CH}_3)_3\text{N}$ and $(\text{SiH}_3)_3\text{N}$ molecules which are found to have different geometries.

1. Which is the correct relation of bond angles?

- (1) $\text{NH}_3 > (\text{CH}_3)_3\text{N} > (\text{SiH}_3)_3\text{N}$
 (2) $(\text{SiH}_3)_3\text{N} > (\text{CH}_3)_3\text{N} > \text{NH}_3$
 (3) $\text{NH}_3 > (\text{SiH}_3)_3\text{N} > (\text{CH}_3)_3\text{N}$
 (4) $(\text{CH}_3)_3\text{N} > (\text{SiH}_3)_3\text{N} > \text{NH}_3$

2. Shape of $(\text{SiH}_3)_3\text{N}$ with respect to N is

- (1) Pyramidal (2) T-shaped
 (3) Trigonal planar (4) Tetrahedral

3. Which of the following has highest basic character?

- (1) NH_3 (2) $(\text{CH}_3)_2\text{NH}$
 (3) $(\text{CH}_3)_3\text{N}$ (4) $(\text{SiH}_3)_3\text{N}$

Paragraph 2

Solid N_2O_5 exists as $\text{NO}_2^\oplus \text{NO}_3^\ominus$ and hence is called nitronium nitrate.

4. The gas which is acidic in nature is

- (1) NO (2) N_2O
 (3) NO_2 (4) Both (a) and (b)

5. Which of the following statement is correct for the oxides of nitrogen?

- (1) Dinitrogen trioxide dissolves in potassium hydroxide forming potassium nitrate.
 (2) Aqueous solution of nitrogen dioxide behaves both as a reducing agent and as an oxidising agent.
 (3) NO_2 is non-planar.
 (4) Nitrous oxide is fairly soluble in cold water and turns blue litmus red.

6. Choose the incorrect statement:

- (1) NO_2 molecule is angular with N—O distance equal to intermediate distance between a single and a double bond.
 (2) In N_2O_4 the N—N bond length is longer than the usual N—N single bond distance.
 (3) N_2O is a linear molecule and has a small dipole moment.
 (4) None of these

Paragraph 3

PCl_5 has trigonal pyramidal geometry with sp^3d hybridisation in gases and liquid state but in solid state it exists as ionic compound.

7. The hybridisation of P and shape of POCl_3 are

- (1) sp^3 , tetrahedral (2) sp^3d , distorted tetrahedral
(3) sp^3d , square planar (4) sp^3 , pyramidal

8. In presence of small amount of water, PCl_5 hydrolyses to form

- (1) PCl_3 (2) H_3PO_3
(3) POCl_3 (4) POCl

9. In crystalline state PCl_5 exists as

- (1) $[\text{PCl}_3]^{2+} + 2\text{Cl}^-$ (2) $[\text{PCl}_4]^+ [\text{PCl}_6]^-$
(3) $[\text{PCl}_4]^+ \text{Cl}^-$ (4) $[\text{PCl}_6]^+ [\text{PCl}_4]^-$

10. What is the hybridisation state of cation part of solid PCl_5 ?

- (1) sp^3d^2 (2) sp^3d
(3) sp^3 (4) sp^2

Paragraph 4

The pronounced change from non-metallic to metallic behaviour and also increase in the basicity of oxides from nitrogen to bismuth in group 15 is principally due to increasing size of the atoms. The ionisation potential of nitrogen is very high on account of its small size. However, ionisation potential decreases regularly on descending the group.

11. Which one of the following is a strongest base?

- (1) PH_3 (2) SbH_3
(3) AsH_3 (4) NH_3

12. Among the trihalides of nitrogen, which one is least basic?

- (1) NF_3 (2) NI_3
(3) NBr_3 (4) NCl_3

13. Which one of the following fluorides does not exist?

- (1) NF_5 (2) SbF_5
(3) AsF_5 (4) PF_5

14. Which of the following oxides is most acidic?

- (1) Bi_2O_3 (2) P_2O_3
(3) As_2O_3 (4) Sb_2O_3

15. The most unstable hydride is

- (1) NH_3 (2) SbH_3
(3) BiH_3 (4) PH_3

16. In all the group 15 elements, the number of unpaired electrons in the valence shell is

- (1) 2 (2) 3
(3) 4 (4) 5

17. Which trihalide is most ionic among the following?

- (1) NCl_3 (2) PCl_3
(3) BiF_3 (4) SbF_3

Paragraph 5

Phosphorus forms a number of oxoacids which differ in their structures and oxidation state of phosphorus. All the acids contain phosphorus atom/atoms linked tetrahedrally to four

other atoms or groups. Each of them has at least one $\text{P}=\text{O}$ or $\text{P} \rightarrow \text{O}$ unit and one $\text{P}-\text{OH}$ unit. The OH group is ionisable but H atom linked directly to P is non-ionisable. Structures of all the acids are considered to be derived either from phosphorus acid or phosphoric acid.

18. Which one is monobasic acid?

- (1) H_3PO_2 (2) H_3PO_3
(3) H_3PO_4 (4) H_3PO_5

19. Which one has +3 oxidation state?

- (1) H_3PO_4 (2) H_3PO_3
(3) $\text{H}_4\text{P}_2\text{O}_7$ (4) $\text{H}_4\text{P}_2\text{O}_6$

20. The acid which forms two series of salts is

- (1) H_3PO_4 (2) H_3PO_3
(3) HPO_3 (4) H_3PO_2

21. Which of the following is a cyclic oxoacid?

- (1) $\text{H}_4\text{P}_2\text{O}_7$ (2) $\text{H}_4\text{P}_2\text{O}_6$
(3) $\text{H}_4\text{P}_3\text{O}_9$ (4) $\text{H}_5\text{P}_5\text{O}_{15}$

22. The number of $\text{P}=\text{O}$ and $\text{P}-\text{O}-\text{H}$ bonds in H_3PO_4 are

- (1) 3, 1 (2) 2, 2
(3) 1, 2 (4) 1, 3

Matrix Match Type

This section contains questions each with two columns—I and II. Match the items given in column I with that in column—II.

	Column I		Column II
1.	(1) Superphosphate of lime	p.	N_2O
	(2) Laughing gas	q.	N_2
	(3) Inert gas	r.	NH_4Cl
	(4) Sal ammoniac	s.	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

	Column I		Column II
2.	(1) Anhydride of HNO_3	p.	Phosphorous trioxide
	(2) Anhydride of HNO_2	q.	Phosphorous pentoxide
	(3) Anhydride of HPO_3	r.	Nitrogen pentoxide
	(4) Anhydride of H_3PO_3	s.	Nitrogen trioxide

	Mixture		Solution used for separation
3.	(1) PH_3 and NH_3	p.	H_2SO_4
	(2) N_2 and NH_3	q.	Ammoniacal CuCl
	(3) N_2 and Co	r.	Water
	(4) N_2 and O_2	s.	Pyrogallol

	Column I		Column II
4.	(1) Dibasic acid	p.	Phosphorous acid
	(2) Tribasic acid	q.	Ammonium nitrate
	(3) Monobasic acid	r.	Orthophosphoric acid
	(4) Freezing salt	s.	Hypophosphorous acid

5.

	Column I		Column II
(1)	Acid hydride of N	p.	Nitrogen dioxide
(2)	Basic hydride of N	q.	Ammonia
(3)	Brown coloured gas	r.	Hydrazoic acid
(4)	Colourless gas	s.	Nitric oxide

6.

	Column I		Column II
(1)	Salammoniac	p.	Ammonia
(2)	Haber process	q.	Ammonium chloride
(3)	Ostwald's process	r.	$\text{NH}_4\text{NO}_3 + \text{CaCO}_3$
(4)	Nitrochalk	s.	Nitric acid

7.

	Column I		Column II
(1)	Hypophosphorous acid	p.	$\text{H}_4\text{P}_2\text{O}_7$
(2)	Phosphorous acid	q.	H_3PO_4
(3)	Phosphoric acid	r.	H_3PO_3
(4)	Pyrophosphoric acid	s.	H_3PO_2

8.

	Column I (Reactions)		Column II (Products)
(1)	Hg and Pb with dil HNO_3	p.	Metal nitrates + H_2

(2)	Zn, Fe and Sn with very dil. HNO_3	q.	Metal nitrates + NH_2OH or NH_4NO_3
(3)	Zn, Fe and Sn with dil. HNO_3	r.	Metal nitrates + NO
(4)	Mg, Mn and Ca with dil. HNO_3	s.	Metal nitrates + N_2O

9.

	Column I (Reactions)		Column II (Products)
(1)	Cu, Ag, Hg, Pb and Zn with conc. HNO_3	p.	H_2SnO_3 and NO_2
(2)	Fe with moderately conc. HNO_3	q.	Metal nitrates + NO_2
(3)	Fe, Al, Co, Ni and Cr with conc. HNO_3	r.	Ferric nitrate + NO_2
(4)	Sn with conc. HNO_3	s.	Rendered passive

10.

	Column I		Column II
(1)	Phosphorite	p.	$3\text{Ca}_3(\text{PO}_4)_2\text{CaCl}_2$
(2)	Chloroapatite	q.	$3\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2$
(3)	Fluoroapatite	r.	CAN
(4)	Nitrochalk	s.	$\text{Ca}_3(\text{PO}_4)_2$

11. Match the items given in Column I with that in Column II and III

	Column I		Column II		Column III
	Oxides of nitrogen		Method of preparation		Characteristics
(1)	N_2O	i.	$\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{PbO} + \text{O}_2 + \dots\dots\dots$ LiNO_3 and $\text{Mg}(\text{NO}_3)_2$, also give same reaction.	p.	Colourless, neutral gas. On heating at 600°C , gives $\text{N}_2 + \text{O}_2$
(2)	NO	ii.	$4\text{AgNO}_3 + 2\text{Cl}_2 \longrightarrow 4\text{AgCl} + \text{O}_2 + \dots\dots\dots$	q.	Colourless gas, in solid and liquid state it is blue in colour. On heating at 1100°C , gives $\text{N}_2 + \text{O}_2$
(3)	NO_2	iii.	$\text{NH}_4\text{NO}_3 \xrightarrow{250^\circ\text{C}} \dots\dots\dots + 2\text{H}_2\text{O}$	r.	It is an hydride of HNO_3 and acidic in nature. In solid state, it exists as: $[\text{NO}_2]^+ [\text{NO}_3]^-$
(4)	N_2O_5	iv.	Catalytic oxidation of NH_3 . $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt}} \dots\dots\dots + 6\text{H}_2\text{O}$	s.	Brown gas highly reactive and paramagnetic. Acts as an oxidising agent.

12. Match the items given in Column I with that in Column II and III

	Column I		Column II		Column III
	Different concentration of HNO_3		Elements		Main products
(1)	Conc. HNO_3	i.	Fe, Al, CO, Ni, and Cr	p.	Complex ions + $\text{NO}(\text{g})$
(2)	Dil. HNO_3	ii.	Cu, Ag, Hg, Pb and Zn	q.	Rendered passive
(3)	Cold dil. HNO_3	iii.	Noble metals like Au, Pt	r.	Metal nitrates + $\text{NO}(\text{g})$
(4)	Aqua regia	iv.	Cu, Ag, Hg and Pb	s.	Metal nitrates + $\text{NO}_2(\text{g})$
		v.	Mg and Mn	t.	Metal nitrates + $\text{H}_2(\text{g})$

For Q. 13 to Q. 16:

Answer the questions given below by appropriately matching the information given in three Column of the following table.

	E.C. of 15 group elements		Characteristics (I)		Characteristics (II)
(1)	$6s^2 6p^3$	i.	Metalloid	p.	Least stable hydride.
(2)	$3s^2 3p^3$	ii.	Basic oxides and metallic in character	q.	Exists in tetrahedral tetra-atomic forms and are solid
(3)	$4s^2 4p^3$	iii.	Its hydride have highest bond angle amongst other hydrides	r.	Do not form sulphides
(4)	$2s^2 2p^3$	iv.	Graham salt	s.	Shows inert pair effect

13. For the element nitrogen, CORRECT combination is:

- (1) b—iv—q (2) b—iv—q,s
(3) d—iii—r (4) d—iv—q,s

14. For the element phosphorous, CORRECT combination is:

- (1) b—iv—q (2) b—iv—q,s
(3) d—iii—r (4) d—iv—q,s

15. For the element arsenic, CORRECT combination is:

- (1) b—iv—q,s (2) b—iv—s
(3) c—i—q (4) c—i—q,s

16. For the element bismuth, CORRECT combination is:

- (1) a—ii—p,q,s (2) a—ii—p,q
(3) a—ii—p (4) a—i—p,q,s

Numerical Value Type

- How many nitrogen oxides are known?
- How many lone pairs are present in nitrogen molecule?
- In group 15 elements, the number of unpaired electrons in valence shell is _____.
- How many P—O—P bonds are present in P_4O_8 ?
- In solid PCl_5 molecule, how many P—Cl bonds are present in the cation?
- What is the basicity of pyrophosphoric acid?
- How many σ -bonds are present in N_2O_3 ?
- When excess of ammonia and chlorine react, nitrogen and ammonium chloride are formed. Write the balanced equation and find out how many ammonium chloride molecules are involved in the balanced equation?
- What is the atomicity of phosphorous?
- How many N—O (σ) bonds are present in N_2O_5 ?
- In P_4O_{10} , how many oxygen atoms are bonded to each phosphorous atoms?
- How many unpaired electrons are present in NO molecule?
- The number of vacant orbitals in the valence shell of phosphorous is _____.
- How many hydrogen bonds are formed by each H_3PO_4 molecule?
- On hydrolysis, of calcium phosphide, how many moles of phosphine are formed?

- How many lone pairs are present in white phosphorous?
- How many bridging oxygen atoms are present in P_4O_{10} ?
- How many moles of H_3PO_4 are obtained on hydrolysis of one mole of P_4O_8 .
- On hydrolysis of magnesium nitride, how many moles of ammonia are produced?
- How many electrons are present in the valence shell of P in PCl_3 ?
- The following oxides of nitrogen are given:
(i) N_2O (ii) NO (iii) N_2O_3
(iv) NO_2 (v) N_2O_4 (vi) N_2O_5
If X is the number of neutral oxide and Y is the number of paramagnetic oxide then find the value of $\frac{(X+Y)^2}{5}$.

22. In the following compounds

- (i) P_4O_{10} (ii) Solid PI_5

Calculate the value of $\left(\frac{X+Y}{6}\right)$.

If X is the total number of sp^3 hybridised atoms in both above compounds Y is the total number of sp^2 hybridised atoms in both above compounds.

Archives

JEE MAIN

Single Correct Answer Type

- Which one of the following properties is not shown by NO ?
(1) It is diamagnetic in gaseous state
(2) It is a neutral oxide
(3) It combines with oxygen to form nitrogen dioxide
(4) Its bond order is 2.5 (JEE Main 2013)
- Which of the following statements is wrong?
(1) The stability of hydrides increases from NH_3 to BiH_3 in group 15 of the periodic table
(2) Nitrogen can't form $d\pi-p\pi$ bond
(3) Single N—N bond is weaker than the single P—P bond
(4) N_2O_4 has two resonance structure. (JEE Main 2014)
- Statement I:** Nitrogen and Oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.
Statement II: The reaction between nitrogen and oxygen requires high temperature.
(1) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.
(2) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion.
(3) The assertion is incorrect, but the reason is correct.
(4) Both are assertion and reason are incorrect. (JEE Main 2015)
- The reaction of zinc with dilute and concentrated nitric acid, respectively produces:

- (1) NO_2 and N_2O (2) N_2O and NO_2
 (3) NO_2 and NO (4) NO and N_2O

(JEE Main 2016)

5. The compound that does not produce nitrogen gas by the thermal decomposition is

- (1) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (2) NH_4NO_2
 (3) $(\text{NH}_4)_2\text{SO}_4$ (4) $\text{Ba}(\text{N}_3)_2$

(JEE Main 2018)

JEE ADVANCED**Single Correct Answer Type**

1. The reaction of P with X leads selectively to P_4O_6 . X is

- (1) dry O_2
 (2) a mixture of O_2 and N_2
 (3) moist O_2
 (4) O_2 in the presence of aqueous NaOH (IIT-JEE 2009)

2. Extra pure N_2 can be obtained by heating

- (1) NH_3 with CuO (2) NH_4NO_3
 (3) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (4) $\text{Ba}(\text{N}_3)_2$

(IIT-JEE 2011)

3. The reaction of white phosphorous with aqueous NaOH gives phosphine along with another phosphorous containing compound. The reaction type; the oxidation state of phosphorous in phosphine and in the other products are, respectively,

- (1) redox reaction; -3 and -5
 (2) redox reaction; +3 and +5
 (3) disproportionation reaction; -3 and +5
 (4) disproportionation reaction; -3 and +3

(IIT-JEE 2012)

4. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen?

- (1) HNO_3 , NO , NH_4Cl , N_2
 (2) HNO_3 , NO , N_2 , NH_4Cl
 (3) HNO_3 , NH_4Cl , NO , N_2
 (4) NO , HNO_3 , NH_4Cl , N_2

(IIT-JEE 2012)

5. The product formed in the reaction of SOCl_2 (thionyl chloride) with white phosphorous is

- (1) PCl_3 (2) SO_2Cl_2
 (3) SCl_2 (4) POCl_3

(JEE Advanced 2014)

6. The order of the oxidation state of the phosphorus atom in H_3PO_2 , H_3PO_4 , H_3PO_3 and $\text{H}_4\text{P}_2\text{O}_6$ is

- (1) $\text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2$
 (2) $\text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6$
 (3) $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_4$
 (4) $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6$

(JEE Advanced 2017)

Multiple Correct Answers Type

1. The nitrogen oxide(s) that contains N—N bond is/are

- (1) N_2O (2) N_2O_3
 (3) N_2O_4 (4) N_2O_5 (IIT-JEE 2010)

2. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10}

- (1) can also be prepared by reaction of P_4 and HNO_3
 (2) is diamagnetic
 (3) contains one N—N bond
 (4) react with Na metal producing a brown gas

(JEE Advanced 2016)

3. The compound(s) which generate(s) N_2 gas upon thermal decomposition below 300°C is (are)

- (1) NH_4NO_3 (2) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
 (3) $\text{Ba}(\text{N}_3)_2$ (4) Mg_3N_2

(JEE Advanced 2018)

4. Based on the compounds of group 15 elements, the correct statement(s) is (are)

- (1) Bi_2O_5 is more basic than N_2O_5
 (2) NF_3 is more covalent than BiF_3
 (3) PH_3 boils at lower temperature than NH_3
 (4) N—N single bond is stronger than the P—P single bond

(JEE Advanced 2018)

Linked Comprehension Type**Paragraph 1**

There are some deposits of nitrates and phosphates in the earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under laboratory conditions but microbes do it easily. Ammonia forms a large number of complexes with transition metal ions. Hybridisation easily explains the ease of sigma donation capability of NH_3 and PH_3 . Phosphine is a flammable gas and is prepared from white phosphorus.

1. Which of the following statements is correct?

- (1) Phosphates have no biological significance in humans.
 (2) Between nitrates and phosphates, phosphates are less abundant in earth's crust.
 (3) Between nitrates and phosphates, nitrates are less abundant in earth's crust.
 (4) Oxidation of nitrates is possible in soil.

2. Which of the following statements is correct?

- (1) Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies spherical s-orbital and is less directional.
 (2) Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies sp^2 -orbital and is more directional.

- (3) Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 -orbital and is more directional.
- (4) Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies spherical s -orbital and is less directional.
3. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a
- (1) dimerisation reaction
 - (2) disproportionation reaction
 - (3) condensation reaction
 - (4) precipitation reaction

(IIT-JEE 2008)

Paragraph 2

Upon heating KClO_3 in the presence of catalytic amount of MnO_2 , a gas W is formed. Excess amount of W reacts with white phosphorus to give X . The reaction of X with pure HNO_3 gives Y and Z .

4. W and X are, respectively

- (1) O_3 and P_4O_6
- (2) O_2 and P_4O_{10}
- (3) O_3 and P_4O_{10}
- (4) O_2 and P_4O_6

5. Y and Z are, respectively

- (1) N_2O_4 and H_3PO_3
- (2) N_2O_4 and HPO_3
- (3) N_2O_5 and HPO_3
- (4) N_2O_3 and H_3PO_4

(JEE Advanced 2017)

Matrix Match Type

1. Match each of the reactions given in Column I with the corresponding product(s) given in Column II.

	Column I		Column II
(a)	$\text{Cu} + \text{dil HNO}_3$	p.	NO
(b)	$\text{Cu} + \text{conc HNO}_3$	q.	NO_2
(c)	$\text{Zn} + \text{dil HNO}_3$	r.	N_2O
(d)	$\text{Zn} + \text{conc HNO}_3$	s.	$\text{Cu}(\text{NO}_3)_2$
		t.	$\text{Zn}(\text{NO}_3)_2$

Numerical Value Type

1. What is the total number of diprotic acids among the following?

H_3PO_4 , H_2SO_4 , H_3PO_3 , H_2CO_3 , $\text{H}_2\text{S}_2\text{O}_7$, H_3BO_3 , H_3PO_2 , H_2CrO_4 , H_2SO_3

(IIT-JEE 2010)

2. Among the following, the number of compounds that can react with PCl_5 to give POCl_3 is

O_2 , CO_2 , SO_2 , H_2O , H_2SO_4 , P_4O_{10}

(IIT-JEE 2011)

3. The total number of compounds having at least one bridging oxo group among the molecules given below is

N_2O_3 , N_2O_5 , P_4O_6 , P_4O_7 , $\text{H}_4\text{P}_2\text{O}_5$, $\text{H}_5\text{P}_3\text{O}_{10}$, $\text{H}_2\text{S}_2\text{O}_3$, $\text{H}_2\text{S}_2\text{O}_5$

(JEE Advanced 2013)

Answers Key

EXERCISES

Single Correct Answer Type

1. (1) 2. (2) 3. (3) 4. (2) 5. (4)
6. (2) 7. (1) 8. (2) 9. (2) 10. (1)
11. (4) 12. (2) 13. (2) 14. (1) 15. (1)
16. (2) 17. (2) 18. (4) 19. (4) 20. (1)
21. (1) 22. (1) 23. (4) 24. (1) 25. (2)
26. (1) 27. (1) 28. (1) 29. (3) 30. (4)
31. (2) 32. (2) 33. (3) 34. (4) 35. (4)
36. (3) 37. (2) 38. (2) 39. (4) 40. (1)
41. (1) 42. (2) 43. (2) 44. (2) 45. (1)
46. (3) 47. (3) 48. (1) 49. (3) 50. (1)
51. (3) 52. (1) 53. (4) 54. (1) 55. (2)
56. (2) 57. (1) 58. (3) 59. (2) 60. (3)
61. (4) 62. (3) 63. (3) 64. (4) 65. (2)
66. (3) 67. (3) 68. (3) 69. (4) 70. (3)
71. (3) 72. (3) 73. (3) 74. (3) 75. (2)
76. (1) 77. (1) 78. (4) 79. (1) 80. (1)
81. (3) 82. (3) 83. (1) 84. (1) 85. (4)
86. (1) 87. (2) 88. (2) 89. (1) 90. (1)
91. (3) 92. (2) 93. (4) 94. (4) 95. (3)
96. (1) 97. (1) 98. (1) 99. (1) 100. (4)
101. (1) 102. (1) 103. (2) 104. (4) 105. (1)
106. (1) 107. (2) 108. (2) 109. (2) 110. (1)
111. (2) 112. (4) 113. (1) 114. (4) 115. (1)
116. (3) 117. (3)

Multiple Correct Answers Type

1. (1, 2, 4) 2. (1, 2, 4) 3. (1, 2, 4) 4. (1, 2) 5. (1, 4)
6. (2, 4) 7. (3, 4) 8. (1, 2) 9. (1, 2, 3) 10. (3, 4)
11. (2, 3, 4) 12. (1, 2, 3, 4) 13. (1, 2, 3) 14. (1, 3, 4) 15. (1, 3)
16. (1, 2, 3, 4) 17. (1, 2, 4) 18. (2, 3) 19. (1, 2, 3) 20. (1, 2)
21. (1, 2, 3) 22. (1, 2, 3) 23. (1, 3) 24. (2, 3) 25. (3, 4)
26. (3, 4) 27. (2, 3, 4) 28. (2, 3) 29. (1, 2) 30. (2, 3)
31. (2, 3) 32. (2, 4) 33. (1, 3) 34. (4) 35. (1, 2, 4)
36. (1, 3, 4) 37. (1, 2) 38. (1, 2, 3)

Linked Comprehension Type

1. (2) 2. (3) 3. (3) 4. (3) 5. (2)
6. (4) 7. (1) 8. (3) 9. (2) 10. (3)
11. (4) 12. (1) 13. (1) 14. (2) 15. (3)
16. (2) 17. (3) 18. (1) 19. (2) 20. (3)
21. (3) 22. (4)

Matrix Match Type

Q. No.	(a)	(b)	(c)	(d)
1.	s	p	q	r

2.	r	s	q	p
3.	r	p	q	s
4.	p	r	s	q
5.	r	q	p	s
6.	q	p	s	r
7.	s	r	q	p
8.	r	q	s	p
9.	q	r	s	p
10.	s	p	q	r
11.	iii-p	iv-q	i-s	ii-r
12.	i, ii-q, s	iv-r,	v-t,	iii-p

13. (c) 14. (b) 15. (d) 16. (a)

Numerical Value Type

1. (5) 2. (2) 3. (3) 4. (6) 5. (4)
6. (4) 7. (4) 8. (6) 9. (4) 10. (6)
11. (4) 12. (1) 13. (5) 14. (4) 15. (2)
16. (4) 17. (6) 18. (2) 19. (2) 20. (8)
21. (3.2) 22. (2.5)

ARCHIVES

JEE Main

Single Correct Answer Type

1. (1) 2. (1) 3. (1) 4. (2) 5. (3)

JEE Advanced

Single Correct Answer Type

1. (2) 2. (4) 3. (3) 4. (2) 5. (1)
6. (1)

Multiple Correct Answers Type

1. (1, 2, 3) 2. (2, 4) 3. (2, 3) 4. (1, 2, 3)

Linked Comprehension Type

1. (3) 2. (3) 3. (2) 4. (2) 5. (2)

Matrix Match Type

1. (a) p, s (b) q, s (c) r, t (d) q, t

Numerical Value Type

1. (6) 2. (4) 3. (6)

3

p-Block Group 16 Elements The Oxygen Family

OVERVIEW

- Group 16 elements are known as **chalcogens**, i.e. ore forming elements.
- General electronic configuration: ns^2np^4
- Oxygen is the most abundant element. Sulphur is the 16th most abundant element. The last member Po is radioactive.
- Oxygen is a gas, while rest of the members are solids.
- Oxygen is diatomic, while other exists as S_8 , Se_8 , Te_8 .
- Atomic radii:** $O < S < Se < Te < Po$
- Ionisation enthalpy:** $O > S > Se > Te > Po$
- Electronegativity:** $O > S > Se > Te > Po$
- Electron gain enthalpy:** $O < S < Se < Te < Po$
- Metallic character:** Increases with increase in atomic number.

O	S	Se	Te	Po
Non-metals		Metalloids		Metal

- Allotropy:** All the members show allotropy
Oxygen: O_2 and O_3
Sulphur: Rhombic, monoclinic, plastic and amorphous
Selenium: Red and grey form
- Oxidation state:** Oxygen because of high electronegativity shows an oxidation state of -2 .
- Catenation:** $O < S > Se > Te > Po$
Catenating ability depends on E-E bond strength (where E = O, S, Se, Te and Po)

14. Oxidation states:

O	S	Se	Te	Po
-2	-2, +2,	-2, +2,	-2, +2,	+2,
	+4, +6	+4, +6	+4, +6	+4, +6

Tendency to show -2 oxidation state decreases down the group. The compounds having $+4$ oxidation state show both oxidising and reducing properties while compounds having $+6$ oxidation states are only oxidising.

- All elements form hydroxides of the type of H_2E , where E = O, S, Se, Te and Po.

- Covalent character:** $H_2O < H_2S < H_2Se < H_2Te$
- Thermal stability:** $H_2O > H_2S > H_2Se > H_2Te$
- Acidic nature:** $H_2O < H_2S < H_2Se < H_2Te$
- Reducing agent:** $H_2O < H_2S < H_2Se < H_2Te$
- Volatility:** $H_2O \gg H_2S > H_2Se > H_2Te$

- Boiling point:** $H_2O (373\text{ K}) > H_2Te (269\text{ K}) > H_2Se (232\text{ K}) > H_2S (213\text{ K})$
- Melting point:** $H_2O (273\text{ K}) > H_2Te (222\text{ K}) > H_2Se (208\text{ K}) > H_2S (188\text{ K})$
- Melting point:** $H_2O (273\text{ K}) > NH_3 (195.2\text{ K}) > HF (190\text{ K})$
- Boiling point:** $H_2O (373\text{ K}) > HF (293\text{ K}) > NH_3 (238.5\text{ K})$

- S, Se and Te form oxides on burning in air of the type MO_2 , e.g., SO_2 , SeO_2 , TeO_2 and PoO_2 .

i. **Acidic strength:** $SO_2 > SeO_2 > TeO_2 > PoO_2$

ii. **Stability:** $SO_2 > SeO_2 > TeO_2 > PoO_2$

S, Se and Te also form trioxides. The trioxides are acidic in nature. **Acidic nature** $SO_3 > SeO_3 > TeO_3$

- Sulphur, selenium and tellurium form similar oxyacids.

H_2SO_3	H_2SeO_3	H_2TeO_3
Sulphurous acid	Selenous acid	Tellurous acid
Salts: Sulphites	Selenites	Tellurites
H_2SO_4	H_2SeO_4	H_2TeO_4
Sulphuric acid	Selenic acid	Telluric acid
Salts: Sulphates	Selenates	Tellurates

Strength increases

Strength increases

- S, Se and Te form hexafluorides of type MF_6 . SF_6 is extremely inert. SeF_6 is slightly reactive while TeF_6 is hydrolysed by water into H_6TeO_6 . Many tetrahalides are known. SF_4 is a gas, SeF_4 is a liquid while TeF_4 is a solid. S, Se, Te and Po form tetrachlorides and bromides while Te and Po form tetraiodides

All elements except Se form stable dichlorides and dibromides.

Dimeric monohalides as S_2F_2 , S_2Cl_2 and S_2Br_2 are known.

- Only S and Se form oxyhalides. They are called thionyl and selenyl halides.

SOF_2 $SOCl_2$ $SOBr_2$ $SeOF_2$ $SeOCl_2$ $SeOBr_2$
They react with water readily.

- It occurs in the atmosphere to the extent of 21% by volume and 23% by mass.

- Oxygen combines nearly with all the elements except inert gases, noble metals and halogens. The binary compounds of

3.2 Inorganic Chemistry

oxygen with other elements are called oxides. However, the compounds of oxygen and fluorine are termed as fluorides, as fluorine is more electronegative than oxygen.

22. O_3 is an allotrope of O_2 .

23. O_3 acts as a powerful oxidising agent. ($O_3 \longrightarrow O_2 + O$) is a good bleaching agent. It bleaches oil, ivory, flour, starch waxes, pulp etc.

24. Mercury is oxidised by ozone to suboxide (Hg_2O) which dissolves in mercury. It starts sticking to glass and loses mobility. The mercury loses its meniscus. This is termed as the **tailing of mercury**.

25. Sulphur forms a number of oxides such as S_2O , SO , S_2O_3 , SO_2 , SO_3 , S_2O_7 and SO_4 . Out of these, SO_2 and SO_3 are important and common.

These act as reducing as well as oxidising agents. In presence of moisture, these act as bleaching agents. The bleaching action is due to reduction. The bleaching is temporary.

26. A large number of oxyacids are known in the case of sulphur either in free state or in the form of salts or both. Oxyacids with S-S links are called thioacids. Acids having sulphur in lower oxidation state belong to -ous series while those having sulphur in higher oxidation state belong to -ic series.

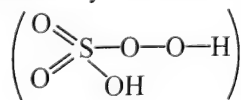
27. **Sulphuric acid (H_2SO_4)**: It is considered as king of chemicals. In ancient days, it was called an oil of **vitriol** as it was obtained by distilling ferrous sulphate (**green vitriol**).

28. **Contact process**: The process involves the conversion of SO_2 into SO_3 by air in presence of a catalyst (platinum or V_2O_5). Best results are obtained when SO_2 and O_2 are present in molecular proportion of 2 : 3. The optimum temperature is $450^\circ C$.

29. H_2SO_4 is a strong dibasic acid and forms two series of salts: (i) bisulphites and (ii) sulphates.

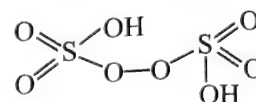
30. **Thiosulphuric acid ($H_2S_2O_3$)**: It is a dibasic acid. It does not exist in free state. Salts are quite stable. Thiosulphates are reducing agents.

31. **Permonoxy sulphuric acid or Caro's acid (H_2SO_5)**: It is a diabasic, stable and crystalline solid. It has a peroxolinkage

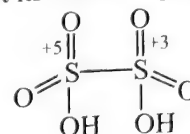


It is a strong oxidising agent.

32. **Peroxydisulphuric acid or Marshall's acid ($H_2S_2O_8$)**: It is a dibasic acid. It has a peroxolinkage. It is a strong oxidising agent.



33. **Dithionic acid ($H_2S_2O_6$)**: It is a dibasic acid. It does not exist in free state but its salts are quite stable.




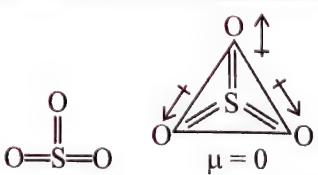
Two S atom are in different oxidation state of +5 and +3.

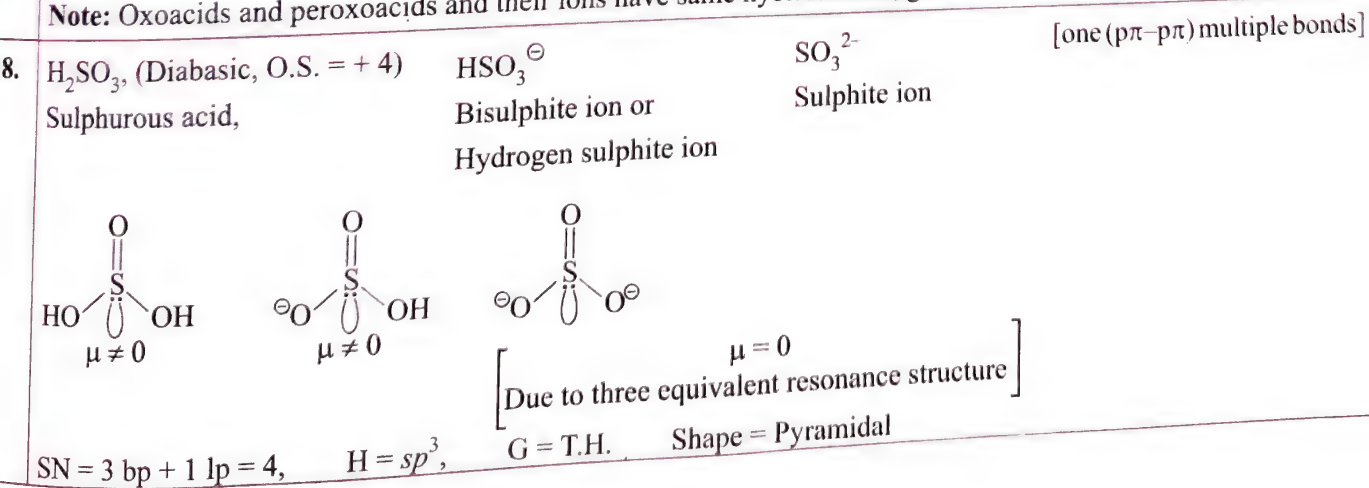
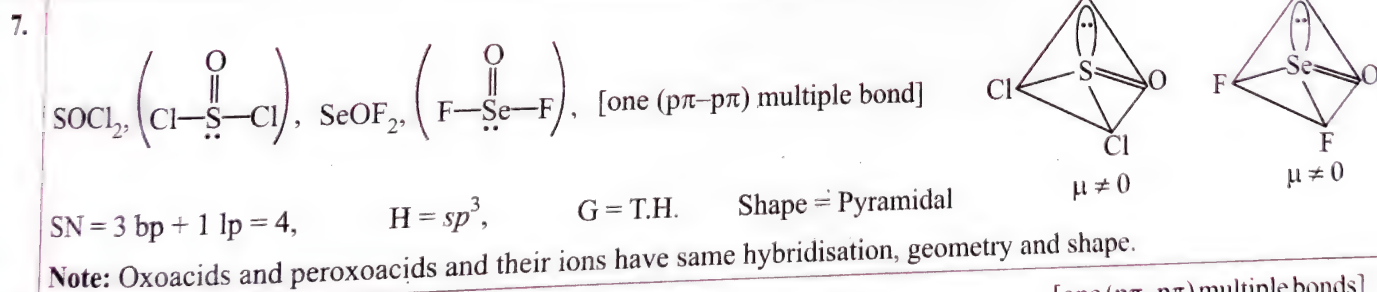
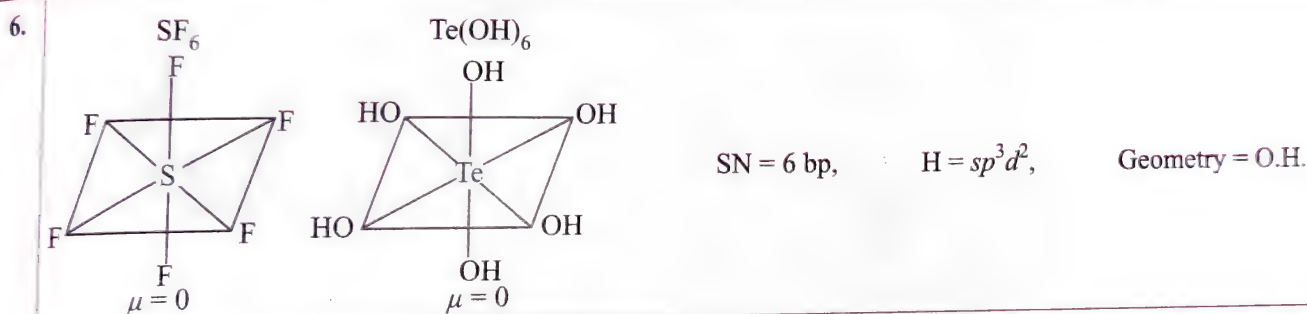
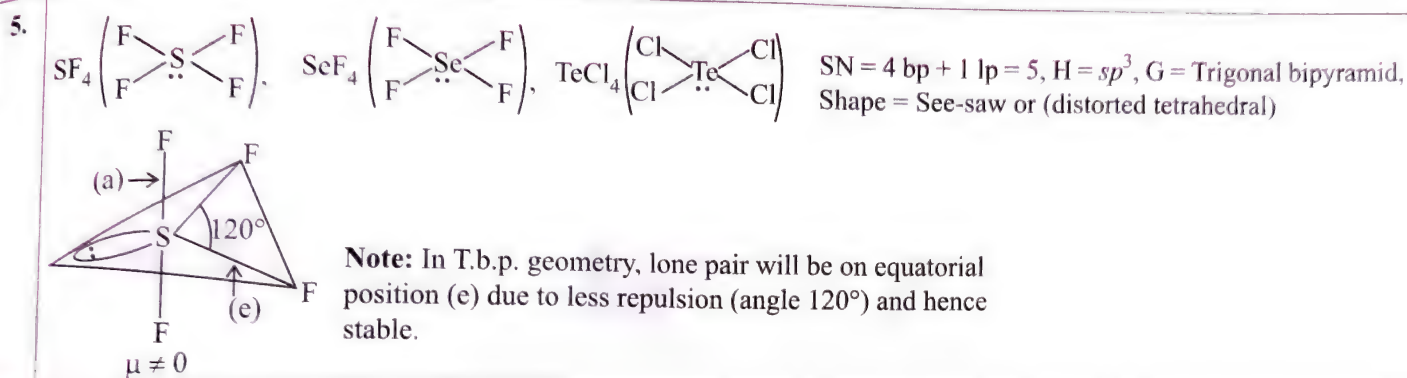
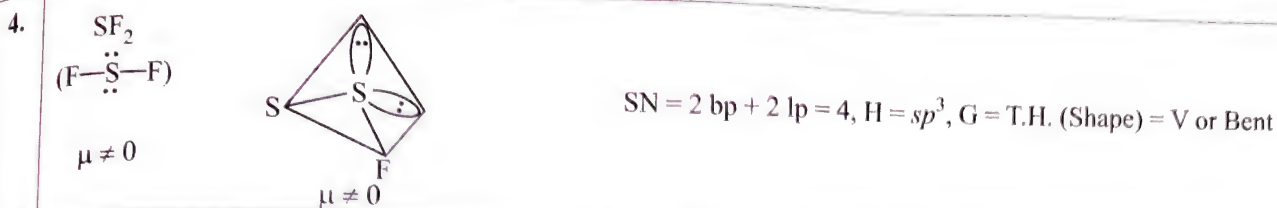
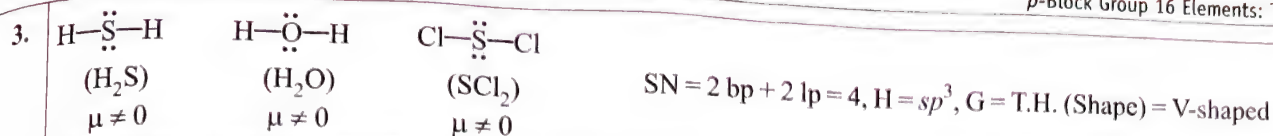
34. **Uses:**

- SF_6 is used in high voltage transformers because of its insulating property.
- Liquid oxygen mixed with finely divided carbon is used in place of dynamite in coal mining.
- A mixture of ozone and cyanogen is used as a rocket fuel.
- Gun powder is a mixture of sulphur, charcoal and KNO_3 .
- S_2Cl_2 is used in the **vulcanisation of rubber**. It is heating rubber with sulphur and was discovered by **Charles Goodyear** in 1839.
- Electrical conductivity of Se is negligible in dark but increases on exposure to light. Due to this property, Se is used in photo-electric cells and as a photoconductor in photocopying (Xerox) machines. It is also used as decolouriser of glass.
- Tellurium is used as an additive in metallurgy for the manufacture of iron, steel, non-ferrous metals and alloys.

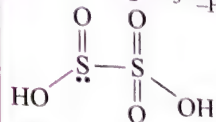
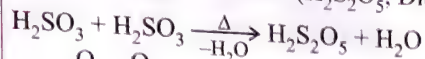
35. The chemical reactions of ozone with oxides of nitrogen and with chlorofluoro-alkanes are responsible for the depletion of ozone shield of the atmosphere. This is called 'ozone hole'. It is feared that this will allow, an excessive amount of UV light to reach the earth which will cause **melanoma** (skin cancer) in humans.

36. Some examples of hybridisation of group 16 ($6e^-$):

1.	SO_2 (Sulphur Dioxide) $O=\ddot{S}=O$ [one ($p\pi-p\pi$) and one ($p\pi-d\pi$) multiple bond] $H = \frac{1}{2}(V+M) = \frac{1}{2}(6+0) = 3$ $SN = 2 \text{ bp} + 1 \text{ lp} = 3$ $H = sp^2$, $G = \text{Planar}$, Shape = V or Bent		$\mu \neq 0$	1($p\pi-p\pi$) multiple bond 1($p\pi-d\pi$) multiple bond
2.	SO_2 (Sulphur trioxide) [one ($p\pi-p\pi$) and two ($p\pi-d\pi$) multiple bond] $H = \frac{1}{2}(V+M) = \frac{1}{2}(6+0) = 3$ $SN = 3 \text{ bp}$ $H = sp^2$, $G = \text{Planar}$		$\mu = 0$	1($p\pi-p\pi$) multiple bond 2($p\pi-d\pi$) multiple bond



9. Di or pyrosulphurous acid ($\text{H}_2\text{S}_2\text{O}_5$, Dibasic, O.S. = +4) [2(p π -d π) multiple bond]



Pyrosulphurous acid



Hydrogen pyrosulphite ion



Pyrosulphite ion

SN = 3 bp + 1 lp = 4,

H = sp^3 ,

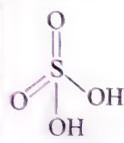
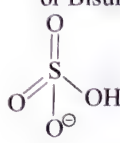
G = T.H.

Shape = Pyramidal

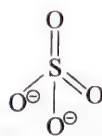
10. Oxo-acids of sulphur: [2 (p π -d π) multiple bonds]



Sulphuric acid

 $\mu \neq 0$ Hydrogen sulphate ion
or Bisulphate ion $\mu \neq 0$ 

Sulphate ion

 $\mu = 0$

[Due to four equivalent structure]

SN = 4 bp,

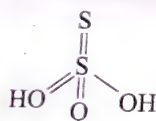
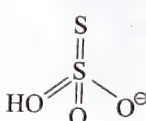
H = sp^3 ,

Geometry = T.H.

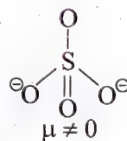
11. Thio sulphuric acid ($\text{H}_2\text{S}_2\text{O}_3$) [2(p π -d π) multiple bond]
(Dibasic, O.S. = +2)



Thiosulphuric acid

 $\mu \neq 0$ Hydrogen-thio-
sulphate ion $\mu \neq 0$ 

Thiosulphate ion

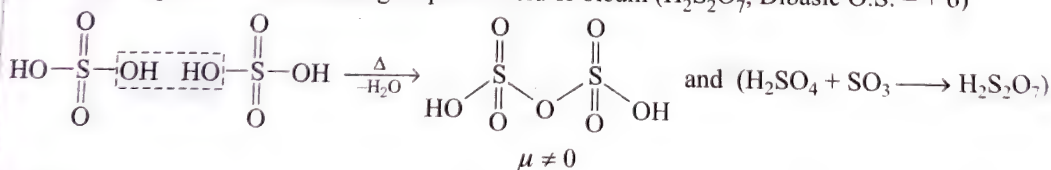
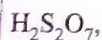
 $\mu \neq 0$

SN = 4 bp,

H = sp^3 ,

Geometry = T.H.

12. Di or Pyrosulphuric acid or fuming sulphuric acid or oleum ($\text{H}_2\text{S}_2\text{O}_7$, Dibasic O.S. = +6)

 $\mu \neq 0$ 

Pyrosulphuric acid



Hydrogen pyrosulphate ion



Pyrosulphate ion

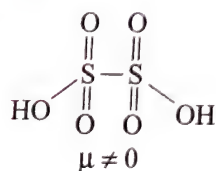
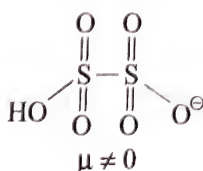
SN = 4 bp,

H = sp^3 ,

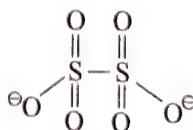
Geometry = T.H.

[4(p π -d π) multiple bond]

13. Dithionic acid ($\text{H}_2\text{S}_2\text{O}_6$) [4(p π -d π) multiple bond]
(Dibasic, O.S. = +5)

 $\mu \neq 0$  $\mu \neq 0$ 

Dithionate ion

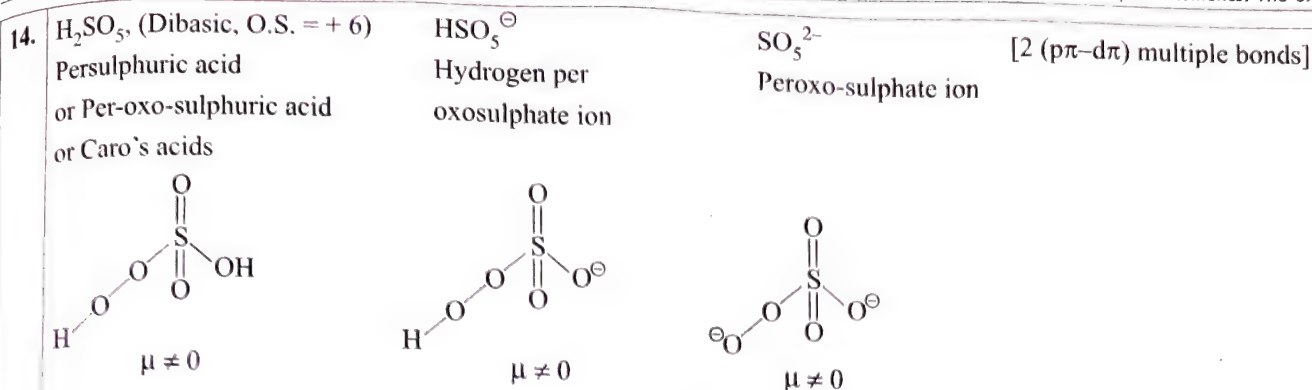
 $\mu = 0$

[Due to three equivalent resonance structure]

SN = 4 bp,

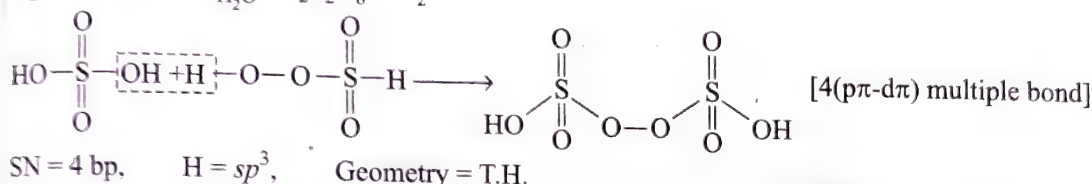
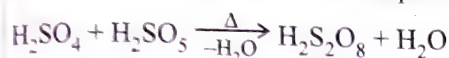
H = sp^3 ,

Geometry = T.H.



SN = 4 bp. $\text{H} = sp^3$, Geometry = T.H.

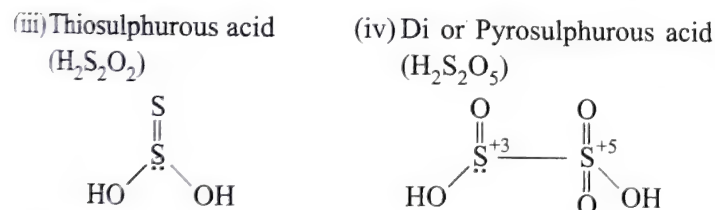
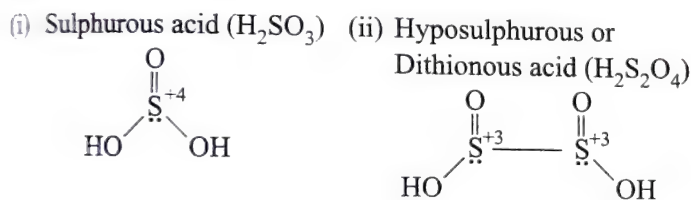
15. Peroxydisulphuric acid or Perdisulphuric acid or Marshall's acid ($\text{H}_2\text{S}_2\text{O}_8$). (Dibasic, O.S. = + 6)



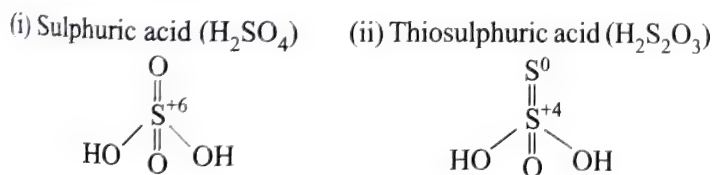
Oxyacids of sulphur are listed in five groups:

1. Sulphoxylic acid (H_2SO_2)

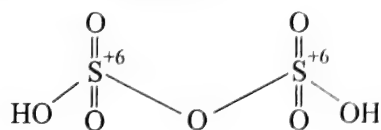
2. Sulphurous acid series:



3. Sulphuric acid series:

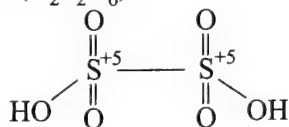


(iii) Pyrosulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$)

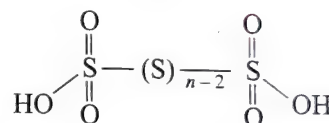


4. Thionic acid series:

(i) Dithionic acid ($\text{H}_2\text{S}_2\text{O}_6$)

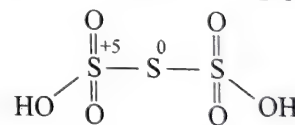


(ii) Polythionic acid ($\text{H}_2\text{S}_n\text{O}_6$)

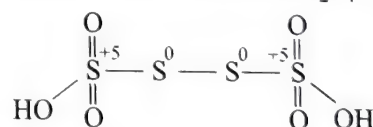


For Example:

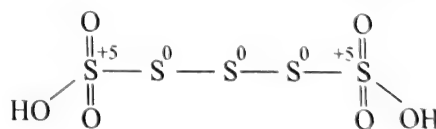
(a) Trithionic acid (when $n = 3$) ($\text{H}_2\text{S}_3\text{O}_6$)



(b) Tetrathionic acid (when $n = 4$) ($\text{H}_2\text{S}_4\text{O}_6$)

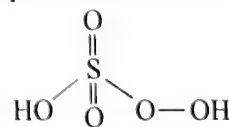


(c) Pentathionic acid (when $n = 5$) ($\text{H}_2\text{S}_5\text{O}_6$) and so on.

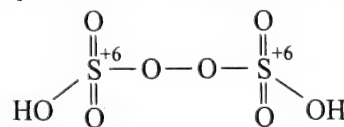


5. Peroxo acid series:

(i) Permonooxo sulphuric acid or Caro's acid (H_2SO_5)



(ii) Peroxodisulphuric acid or Marshall's acid ($\text{H}_2\text{S}_2\text{O}_8$).



3.1 INTRODUCTION

Group 16 elements are known as group of chalcogens. The name is derived from the Greek word for brass and points to the association of sulphur (S) and its congeners with copper (Cu). Most Cu minerals contain either oxygen or sulphur and frequently the other members of the group.

3.2 ABUNDANCE AND OCCURRENCE

Oxygen is the most abundant of all the elements. It occurs in the free form as dioxygen molecule (O_2) and makes up 20.46% by volume and 23% by mass of the atmosphere. It also occurs in the form of ozone (O_3), an allotrope of oxygen, in the upper atmosphere which protects us from the harmful radiations of the sun.

Oxygen makes up 46.6% by weight of the earth's crust where it mainly occurs as silicate minerals. Oxygen also occurs in many metal oxide ores and as deposits of oxosalts such as carbonates, sulphates, nitrates and borates. It also makes up 89% by weight of water in oceans.

Sulphur, on the other hand, occurs less abundantly. Sulphur is the 16th most abundant element and constitutes 0.03 to 0.1% by mass of earth's crust. It occurs mainly, in the combined state, as sulphates such as gypsum, $CaSO_4 \cdot 2H_2O$; epsom salt, $MgSO_4 \cdot 7H_2O$; baryte, $BaSO_4$ and as sulphides such as galena, PbS ; zinc blende, ZnS and copper pyrites, $CuFeS_2$. Traces of sulphur occur as hydrogen sulphide in volcanoes. Organic materials such as eggs, proteins, garlic, onion, hair, mustard and wool also contain sulphur.

Selenium and tellurium are less abundant than sulphur and occur as selenides and tellurides in sulphide ores. Polonium is even less abundant in the earth crust, where it occurs as decay product in thorium and uranium minerals.

3.3 ATOMIC AND PHYSICAL PROPERTIES

The important atomic and physical properties of group 16 along with electronic configuration are given in Table 3.1 and are discussed in the following sections.

Table 3.1 Atomic and physical properties of group 16 elements

Property	Element				
	Oxygen	Sulphur	Selenium	Tellurium	Polonium
Symbol	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass / ($g\ mol^{-1}$)	16.00	32.06	78.96	127.60	210.00
Electronic configuration	[He] $2s^2 2p^4$	[Ne] $3s^2 3p^4$	[Ar] $3d^{10} 4s^2 4p^4$	[Kr] $4d^{10} 5s^2 5p^4$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$
Covalent radius / (pm) ^a	66	104	117	137	146
Ionic radius / (pm)	140	184	198	221	230 b
Ionisation enthalpy, $\Delta_i H_1$	1314.0	1000	941	869	813
$\Delta_i H_2$ ($\Delta_i H$) / ($kJ\ mol^{-1}$)	3388	2251	2045	1790	—
Electronegativity	3.50	2.44	2.48	2.01	1.76
Electron gain enthalpy ($\Delta_{eg} H^\ominus$) / ($kJ\ mol^{-1}$)	−141	−200	−195	−190	−174
Density ($g\ cm^{-3}$) / 298 K	1.32 ^c	2.06 ^d	4.19 ^e	6.25	—
Melting point / (K)	55	393 ^f	490	725	520
Boiling point / (K)	90	718	958	1260	1235
Oxidation states*	−2, −1, −1, +1, +2	−2, +2, +4, +6	−2, +2, +4, +6	−2, +2, +4, +6	+2, +4

Note: ^a Single bond, ^b Approximate value, ^c At the melting point, ^d Rhombic sulphur, ^e Hexagonal grey,

^f Monoclinic form at 673 K. Oxygen shows oxidation states of +2 and +1 in oxygen fluorides OF_2 and O_2F_2 respectively.

3.3.1 ELECTRONIC CONFIGURATION

General valence shell electronic configuration of 16 elements is $ns^2 np^4$, i.e. they have six electrons in the valency shell. Since the differentiating electron enters in the p -orbital, group 16 elements are also p -block elements. Electronic configuration of group 16 elements is given in Table 3.1.

3.3.2 ATOMIC AND IONIC RADII

The atomic radii of group 16 elements are smaller than those of the corresponding group 15 elements. This is due to increase in effective nuclear charge on moving from group 15 to group 16, which results in greater attraction of the electrons by nucleus.

Consequently atomic radii decreases, e.g. atomic radii of N is more than atomic radii of O.

Down the group (\downarrow), i.e., from O to Po, atomic radii as well as ionic radii (Table 3.1) increase. This increase is primarily due to increase in number of electron shells down the group.

3.3.3 IONISATION ENTHALPY (IE) OR ($\Delta_i H^\ominus$)

Down the group (\downarrow), i.e. from O to Po, ionisation enthalpy decreases. This is due to increasing atomic radii and hence increasing shielding effect of the inner electrons or decreasing effective nuclear charge down the group.

(IE_1 or $\Delta_i H_1^\ominus$): $O > S > Se > Te > Po$

The first ionisation enthalpies ($\Delta_i H_1$) of the group 16 elements are unexpectedly lower while their second ionisation enthalpies ($\Delta_i H_2$) are higher than those of the corresponding group 15 elements.

The first ionisation enthalpy ($\Delta_i H_1$) of group 16 elements is lower than those of group 15 elements despite their smaller atomic radii and higher nuclear charge. This is due to the relatively symmetrical and more stable electronic configuration of group 15 elements as compared to those of group 16 elements.

3.3.4 ELECTRONEGATIVITY (EN)

The electronegativity values of group 16 elements are higher than the corresponding group 15 elements. This is due to smaller atomic radii of group 16 elements as compared to group 15 elements. Oxygen is the second most electronegative element ($EN = 3.5$), the first being fluorine ($EN = 4.0$).

Down the group (\downarrow), electronegativity decreases.

The electronegativity of sulphur is, however, much lower than that of oxygen. This is probably due to an unexpected increase in the size of sulphur (107 pm) as compared to that of oxygen (66 pm). Thereafter, the electronegativity decreases slowly but regularly from selenium to polonium as the size of atom increases slowly but regularly.

Further since after oxygen there is a steep drop in electronegativity of S, Se, Te and Po, therefore, their compounds have less ionic character as compared to those of oxygen.

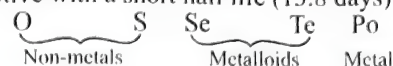
3.3.5 ELECTRON GAIN ENTHALPY ($\Delta_{eg} H^\ominus$)

The elements of group 16 have two electrons less than the nearest noble gas configuration. Therefore, they have a high tendency to accept two additional electrons and hence have large negative electron gain enthalpies next only to the halogens. The electron gain enthalpy of oxygen is, however, **least negative in this group**. This is due to its small size. As a result of which, the electron repulsions in the relatively small $2p$ -subshell are comparatively large and hence the incoming electrons are not accepted with the same ease as in case of other elements of this group.

3.3.6 NON-METALLIC AND METALLIC CHARACTER

Elements of group 16 are less metallic due to high ionisation enthalpy values. Down the group (\downarrow), with the decrease in ionisation enthalpy values, metallic character increases. Thus oxygen and sulphur are typical non-metals. Sulphur acts as an insulator; selenium and tellurium though essentially non-metallic, show some metallic character as well and hence may be called as metalloids. Thus Se and Te behave as semiconductors. The last

member of this group, i.e. polonium is however metallic in nature but is radioactive with a short half life (13.8 days).



3.3.7 MELTING AND BOILING POINTS

Down the group (\downarrow), melting and boiling points increase regularly from oxygen to tellurium. However, melting and boiling points of polonium are lower than those of tellurium.

This is due to the fact that down the group (\downarrow), with the increase in atomic size or atomic mass, van der Waals forces of attraction also increase and hence melting and boiling points increase regularly from oxygen to tellurium. However, at polonium due to maximum number of intervening d - and f -electrons, the inert pair effect exists in Po. Consequently, the ns and np valence electrons in Po are less available and hence van der Waals forces of attraction will be weaker in Po as compared to Te. Hence melting and boiling points of Po will be less than that of Te.

3.3.8 ELEMENTAL STATE

Oxygen exists as a diatomic gas at room temperature while other elements (S, Se and Te) exist as octa-atomic solids. Due to small size and high electronegativity, oxygen atom forms $p\pi-p\pi$ double bond with other oxygen atom to form $O = O$ molecule. The intermolecular forces of attraction between oxygen molecules are weak van der Waals forces and hence oxygen exists as a diatomic gas at room temperature.

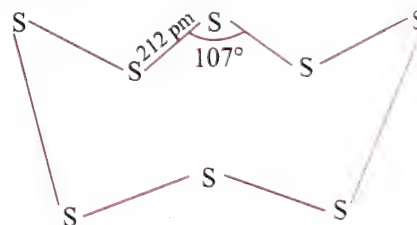


Fig. 3.1 Puckered 8-membered ring structure of sulphur molecule (S_8)

However, the rest of elements of this group do not form $p\pi-p\pi$ multiple bonds due to their larger size and hence do not exist as diatomic (M_2) molecules. Instead they prefer to form single bonds and have complex structures. For example, S, Se and Te exist as octa-atomic molecules (S_8 , Se_8 and Te_8) having puckered 8-membered crown shaped rings (Figure 3.1).

3.3.9 MULTIPLE BONDING

Oxygen forms $p\pi-p\pi$ double bonds but other elements do not. However, S and other elements of this group possess d -orbitals and hence form $p\pi-d\pi$ multiple bonds. To obtain effective $p\pi-d\pi$ overlap, the size of d -orbital must be similar to that of p -orbital. Thus, sulphur forms stronger $p\pi-d\pi$ bonds than the larger elements of this group. Down the group, i.e. from S to Se, tendency to form $p\pi-p\pi$ multiple bond decreases.

3.3.10 CATENATION

The tendency of atoms of the same element to link together to form chains and rings is known as catenation. Amongst group 16 elements, oxygen has lesser catenating ability as compared to sulphur. Further from S to Po, catenating ability decreases. The catenation phenomenon is dependent on E-E bond strength.

Because of stronger S—S bonds as compared to O—O bonds, sulphur has a stronger tendency for catenation than oxygen. This can be explained as follow.

Due to small size, the lone pairs of electrons on the oxygen atoms repel the bond pair of the O—O bond to a greater extent than the lone pairs of electrons on the sulphur atoms in S—S bond. As a result, S—S bond is much stronger (213 kJ mol^{-1}) than O—O bond (138 kJ mol^{-1}) and hence sulphur has a much stronger tendency for catenation than oxygen. Further, as the size of the atom increases down the group from S to Po, the strength of the element–element bond decreases and hence the tendency for catenation decreases accordingly.

3.3.11 ALLOTROPY

The phenomenon by which an element exists in two or more different crystalline or amorphous forms is called allotropy and the different forms are called allotropic forms or allotropes of the given element. Different allotropic forms of an element have different physical properties but similar chemical properties.

Allotropes of oxygen: O_2 (dioxygen) and O_3 (Ozone). (For more details refer to Sections 3.7 and 3.8)

Allotropes of sulphur: Rhombic, monoclinic, plastic and amorphous. (For more details refer to Section 3.10)

Allotropes of selenium: Six allotropes are known. There are three red non-metallic forms containing Se_8 rings. They differ in the way the rings are packed in the crystal. An amorphous red form contains polymeric chains. There are in addition two grey forms. The most stable is the grey metallic forms, which contains infinite spiral chains of Se atoms with weak metallic interaction between adjacent chains. Grey selenium is the only allotrope of selenium which conducts electricity.

Allotropes of tellurium: Tellurium has only one crystalline form, which is silvery white and semi-metallic. It is similar to grey Se, but has stronger metallic interaction.

Allotropes of polonium: Polonium is a true metal. It exists as an α -form which is cubic and a β -form which is rhombohedral. Both forms are metallic. Thus, there is a marked decrease in the number of allotropic forms from S to Se to Te.

Note: Photosensitive elements: The grey form of selenium (metallic) and tellurium consists of parallel chains held by weak metallic bonds. In the presence of light, the weak metallic bonds are excited and as a result, the number of free electrons increases and so does the conductivity. Thus, these elements conduct electricity significantly only in presence of light. That is why Se and Te are called photosensitive elements. Further since conduction increases with intensity of light, selenium is particularly used for measuring the intensity of light

3.4 OXIDATION STATES

O.S. is defined as the residual charge left on the atom where other atoms are removed as ions. Since all the elements of this group have ns^2np^4 configuration in their valence shell (outermost orbit), they can attain noble gas configuration viz. ns^2np^6 either by gaining or by sharing electrons. These elements, therefore, show two types of oxidation state.

1. Negative oxidation state: The high electronegativity of oxygen indicates that it will tend to complete its octet preferably by gaining electron. Because of this, almost all

metal oxides are ionic and contain O^{2-} ions in which oxygen exhibits an oxidation state of -2 .

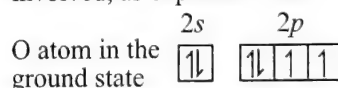
Even if the octet is completed by sharing of electrons, these electrons, for the purpose of determining the oxidation state, are counted towards oxygen because, except OF_2 , oxygen forms the more electronegative atom in all its compounds. Oxygen thus exhibits an oxidation state of -2 .

In addition, oxygen shows an oxidation state of (i) -1 in peroxides such as H_2O_2 , (ii) $-1/2$ in superoxides such as KO_2 and (iii) $+1$ in O_2F_2 and $+2$ in OF_2 .

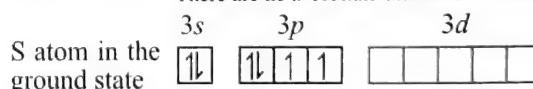
The electronegativity of these elements are, however, low. Their compounds, even with most electropositive elements, are rarely more than 50% ionic.

Since the electronegativities decrease down the group i.e. O to Po, the tendency of elements to show -2 oxidation state decreases down the group from sulphur to polonium. Hence there is much less probability of the formation of the dinegative ions in case of S, Se and Te. The least electronegative element, polonium, in fact does not exhibit negative oxidation state at all. Rather it shows $+2$ oxidation state.

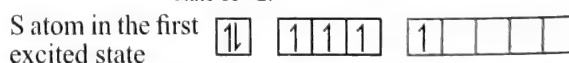
2. Positive oxidation states: Since electronegativity of oxygen is very high, it exhibits only a negative oxidation state. It shows no positive oxidation state, except in O_2F_2 and OF_2 . In the case of other elements, since electronegativities decrease (and also the ionisation energies decrease) down the group towards heavier elements, positive oxidation states become more frequent. The electronic configuration ns^2np^4 for the outer shell suggests that these elements can have three positive oxidation states, viz. $+2$, $+4$ and $+6$. The $+2$ and $+4$ states are shown when only the p -electrons are involved, as explained below.



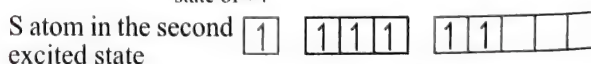
There are no d -orbitals Excitation not easy.



Two unpaired electrons account for an oxidation state of $+2$.



Four unpaired electrons account for an oxidation state of $+4$



Six unpaired electrons account for an oxidation state of $+6$

Except oxygen, all the elements have vacant d -orbitals in their valence shells. In the ground state, they have only two unpaired electrons which permit formation of two bonds. This explains their 2 oxidation state. In the excited state, however, one of the p -electrons goes to the vacant d -orbital of the same shell, thus, making 4 unpaired electrons available for chemical bonding. This accounts for $+4$ oxidation state. Thus, S, Se and Te are tetravalent in their typical compounds with oxygen.

On further excitation, the ns -electrons also get unpaired, thus making 6 unpaired electrons available for bond formation. This explains +6 oxidation state. Thus in their compounds with fluorine, these elements exhibit an oxidation state of +6.

The behaviour of oxygen is different. It belongs to the second period and has only two shells, viz. K and L-shells in its structure. Since the outer L-shell contains only s - and p -orbitals, therefore, oxygen does not have d -orbitals in its valence shell. So, in the case of oxygen, the $2p$ -electrons on excitation have to go to $3s$ -orbital, there being no d -orbitals in L-shell. But since too much energy is required to excite an electron into a higher shell (in this case from L to M-shell), the electrons in oxygen do not get unpaired. Therefore, **oxygen behaves as a divalent element only.**

3.5 CHEMICAL REACTIVITY

1. Oxygen is the most reactive element of the group despite it has high bond dissociation energy of oxygen molecule ($493.4 \text{ kJ mol}^{-1}$) as nearly all its reactions are exothermic. Once initiated, these reactions continue spontaneously. Oxygen directly combines with almost all the metals except noble metals, all the non-metals except noble gases and halogens and many compounds under suitable conditions. The oxides are generally stable compounds. The elements such as W, Pt, Au, halogens and noble gases which do not directly combine with oxygen, form compounds with oxygen indirectly.

2. After oxygen, sulphur is quite reactive element especially at high temperatures which help in breaking of S—S bonds in S_8 molecules. Sulphur burns in air and reacts directly with carbon, phosphorus, arsenic and many metals. Oxidising acids oxidise it into SO_2 and alkalis dissolve it to give sulphides and thiosulphates. It reacts with H_2 and halogens. The sulphides are stable compounds and many metals are found in nature in the form of sulphides.

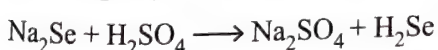
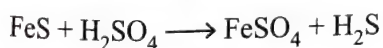
3. However, the reactivity of group 16 elements decreases from oxygen to polonium: $O > S > Se > Te > Po$.

Selenium and tellurium combine with highly electropositive elements such as alkali and alkaline earth metals. Se and Te combine with oxygen, fluorine and chlorine. In general, the compounds of selenium and tellurium are less stable than oxygen and sulphur.

3.5.1 REACTIVITY TOWARDS HYDROGEN—FORMATION OF HYDRIDES

All the elements of group 16 form hydrides having general formula H_2E ; where $E = O, S, Se, Te$ and Po , i.e. H_2O, H_2S, H_2Se, H_2Te and H_2Po .

H_2O is obtained by burning hydrogen in the atmosphere of oxygen, while H_2S, H_2Se and H_2Te are obtained by the action of acids on sulphides, selenides and tellurides.

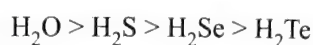


3.5.2 STRUCTURE

All these hydrides have angular shape involving sp^3 -hybridisation of the central atom. The bond angles, however, decrease from H_2O to H_2Te .

Hydride	H_2O	H_2S	H_2Se	H_2Te
Bond angle	104.5°	92.1°	91°	90°

Due to stronger lone pair–lone pair (lp–lp) than bond pair–bond pair (bp–bp) repulsions, the bond angle in water decreases from the tetrahedral value of 109.28° to 104.5° . As we move down the group from O to Te, the size of the central atom goes on increasing and its electronegativity goes on decreasing. As a result, the position of the two bond pairs shifts away and away from the central atom as we move from H_2O to H_2Te . Consequently the repulsions between the bond pairs decrease as we move from H_2O to H_2Te and, therefore, the bond angle decreases in the same order:



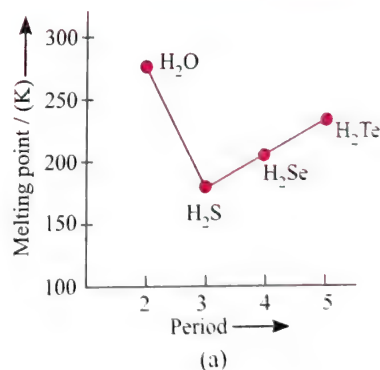
Oxygen forms another important hydride, H_2O_2 .

The bond angles suggest that in H_2S, H_2Se and H_2Te the orbitals used for bonding are close to pure p -orbitals.

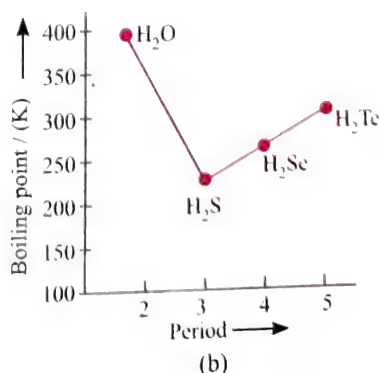
3.5.3 PHYSICAL STATE

Water is colourless, odourless liquid while other hydrides are colourless, poisonous gases with bad odour.

3.5.4 MELTING AND BOILING POINTS



[Melting point: H_2O (373) > H_2Te (222) > H_2Se (208) > H_2S (188) K]



[Boiling point: H_2O (373) > H_2Te (269) > H_2Se (232) > H_2S (213) K]

Fig. 3.2 (a) Melting and (b) boiling points of hydrides of group 16 elements

Explanation of melting and boiling points of hydrides of group 16 elements.

Melting point	Boiling point
The melting point of H_2O is the highest in the hydrides due to intermolecular H-bonding. The H-bonding in H_2O is greater than that of HF and NH_3 . Since the EN of $\text{F} > \text{O} > \text{N}$. But greater H-bonding in H_2O than HF is due to the reason that H_2O forms four H-bonds while HF forms two H-bonds. Hence the increased molecular masses of H_2Te does not affect the melting point of H_2O .	Same explanation as in the melting point.

3.5.5 VOLATILITY

Water has low volatility (high boiling point) as hydrogen bonding brings association. H_2S has high volatility as no hydrogen bonding is present. Volatility decreases from H_2S to H_2Te due to increase in molecular masses of the hydrides.

3.5.6 COVALENT CHARACTER

As the electronegativity difference between E and H decreases, the covalent character of these hydrides increases from H_2O to H_2Te . Water molecule is highly polar. It has high dielectric constant and hence acts as an excellent solvent for inorganic compounds.

Covalent character: $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$

3.5.7 THERMAL STABILITY

The thermal stability decreases as the atomic mass increases. Water dissociates at 2000°C while tellurium hydride, H_2Te , decomposes at room temperature. This is due to an increase in E–H bond length down the group and hence E–H bond becomes weaker and breaks on heating.

Thermal stability: $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$

3.5.8 ACIDIC CHARACTER

This increase in acid strength can be easily explained on the basis of their bond dissociation energy. As the atomic size increases down the group, the bond length increases and hence the bond strength decreases. Consequently, the cleavage of E–H bond ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}, \text{etc.}$) becomes easier. As a result, the tendency to release hydrogen as proton increases, i.e., acid strength increases down the group. Thus, H_2O is least acidic while H_2Po is most acidic.

Acidic character: $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{Po}$

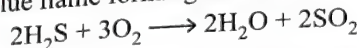
3.5.9 REDUCING NATURE

Hydrides of all elements of group 16 except that of oxygen, i.e., water act as reducing agents. Their reducing character, however, increases from H_2S to H_2Te . This is due to the decrease in their thermal stability. In other words, as the thermal stability decreases, the reducing character increases.

Reducing nature: $\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$

3.5.10 BURNING

H_2S , H_2Se , H_2Te and H_2Po burn in atmosphere of oxygen with blue flame forming dioxides.

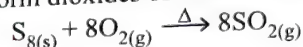


3.5.11 REACTIVITY WITH OXYGEN

All the elements of group 16 form two type of oxides, i.e. EO_2 and EO_3 where $\text{E} = \text{S}, \text{Se}, \text{Te}$ or Po .

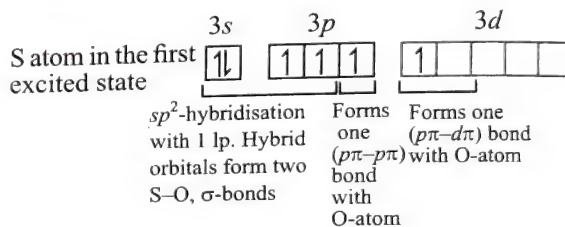
3.5.12 DIOXIDES (EO_2)

Preparation: Sulphur, selenium and tellurium when burnt in air form dioxides of the formula EO_2 .



Structures:

SO_2 : Sulphur dioxide exists as discrete molecules even in the solid state. These molecules are held together by weak van der Waals forces of attraction. Therefore, SO_2 is a gas at room temperature. In SO_2 , S is sp^2 -hybridised. Two of the three sp^2 -orbitals form two σ -bonds with oxygen atoms while the third contains the lone pair of electrons.



Sulphur is now left with one half-filled p -orbital and one half-filled d -orbital. These form one $p\pi-p\pi$ double bond and one $p\pi-d\pi$ double bond with oxygen atoms. Thus, SO_2 has bent (angular) structure. Because of bent structure, SO_2 molecule has a dipole moment of 1.63 D.

The actual bond angle is 119.5° . Despite the fact that two π -bonds are formed due to overlap of different orbitals, the two S–O bonds are, however, equal (143 pm) because of resonance between two structures (I and II) (Figure 3.3).

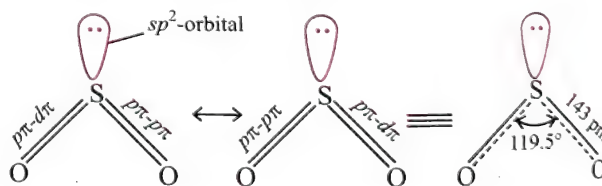


Fig. 3.3 Resonance structures of SO_2

Selenium dioxide is a white crystalline solid. In the gaseous state, it exists as discrete monomeric molecules having structure similar to that of SO_2 [Figure 3.4(a)]. However, in the solid state, it has a non-planar polymeric structure [Figure 3.4 (b)] consisting of infinite chains.

TeO_2 and PoO_2 are non-volatile crystalline ionic solids and each one of these exists in two crystalline forms. TeO_2 in the solid state has a layered structure consisting of TeO_4 units.

The different structures of the dioxides of the elements of group 16 arise due to the fact that the tendency of these elements to form $p\pi-p\pi$ and $p\pi-d\pi$ multiple bonds decreases with increase in atomic size down the group (\downarrow).

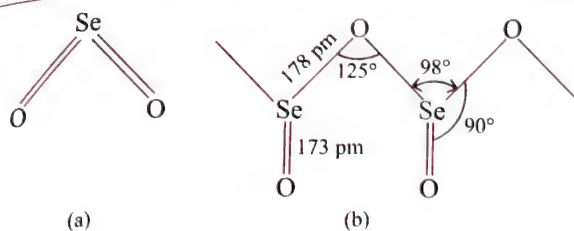


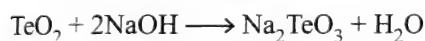
Fig. 3.4 Structures of SeO_2 (a) in the gas phase and (b) linear chain form of solid SeO_2

3.5.13 PROPERTIES OF DIOXIDES

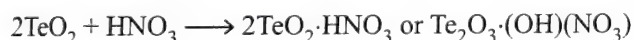
1. **Acid base character:** The dioxides, EO_2 , differ from one another in their reaction with water.

SO_2 dissolves in H_2O giving sulphurous acid (H_2SO_3) which exists only in solution and cannot be isolated.

SeO_2 dissolves giving selenous acid (H_2SeO_3) which can be isolated in the crystalline state. TeO_2 is almost insoluble in water. However, it dissolves both in alkalis to form tellurites and in acids to form basic salts. Thus, TeO_2 is amphoteric in nature. Similarly, PoO_2 is also amphoteric though more basic in character than TeO_2 . Thus, the acidic character of the dioxides of group 16 elements decreases as on moving down the group from S to Po.



Sodium tellurite



Basic nitrate

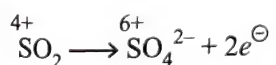
2. **Reducing-oxidising properties:** Since +6 oxidation state of S is more stable than +4, therefore, it acts as a reducing agent. Further, since the stability of +6 oxidation decreases from S to Te, therefore, the reducing character of the dioxides decreases while their oxidising character increases. Thus, TeO_2 acts as an oxidising agent.

ILLUSTRATION 3.1

Reducing property of dioxides decreases from SO_2 to TeO_2 . Why?

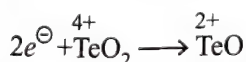
Sol.

i. SO_2 undergoes oxidation to SO_4^{2-} and thus is reducing.



More stable state

ii. TeO_2 undergoes reduction to TeO and thus is oxidising or less reducing. This is due to the inert pair effect. Lower O.S. is more stable down the group.



3.5.14 TRIOXIDES (EO_3)

All the elements of group 16 form trioxides, EO_3 . O_3 and SO_3 are gases. Sulphur in SO_3 is sp^2 -hybridised. The three sp^2 -orbitals of sulphur overlap with p -orbitals of oxygen to form three S—O, σ -bonds. The sulphur atom is now left with one p - and two d -orbitals which overlap with p -orbitals of oxygen to form three π -bonds. However, due to resonance between the three canonical structures (I, II, III), all the three S—O bond lengths are equal (Figure 3.5).

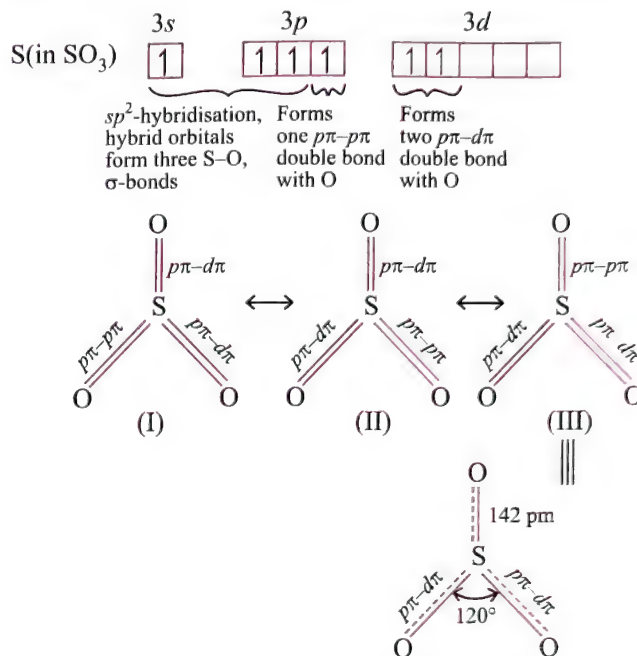
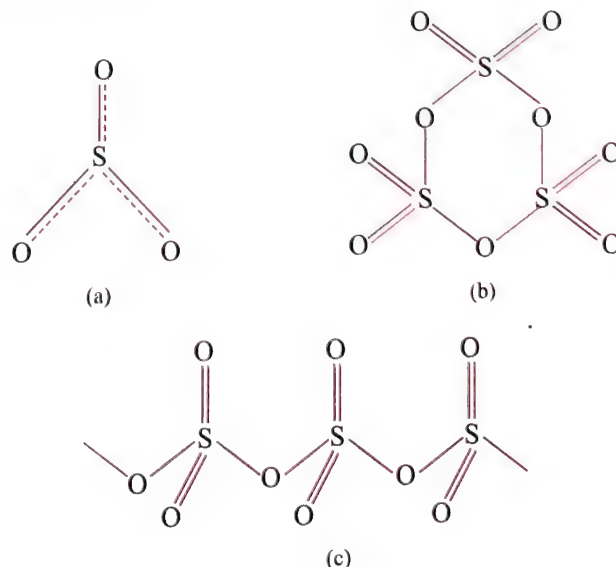


Fig. 3.5 Resonance structures of SO_3

The molecules of SO_3 are held by weak van der Waals forces of attraction. Therefore SO_3 exists as a triangular planar gaseous molecule at room temperature [Figure 3.6(a)] Due to trigonal planar structure, the three S-O dipoles cancel one another. Therefore, the net dipole moment of SO_3 is zero.

However, in the solid state, SO_3 exists in several modifications of which a cyclic trimer [Figure 3.6(b)] or a linear polymeric chain structure [Figure 3.6(c)] are important. SeO_3 , on the other hand, exists as a cyclic tetramer, Se_4O_{12} in the solid state [Figure 3.6(d)].



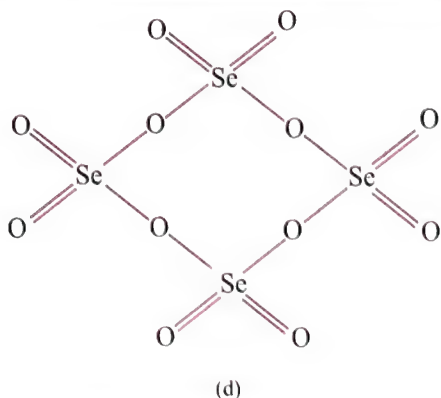
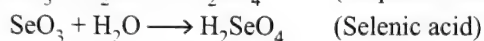
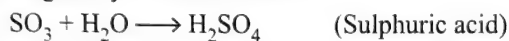


Fig. 3.6 (a) Planar triangular structure of gaseous SO_3 , (b) cyclic trimer of solid SO_3 , (c) linear chain form of solid SO_3 and (d) cyclic tetramer of solid SeO_3

Solid TeO_3 has a network structure in which TeO_6 octahedra share all vertices. All the trioxides are acidic in nature. Acidic nature decreases down the group (\downarrow) with the decrease in electronegativity of central atom.



3.5.15 REACTIVITY TOWARDS HALOGENS—FORMATION OF HALIDES

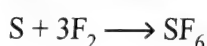
All group 16 elements form compounds with halogens. Since fluorine is more electronegative than oxygen, hence fluorine compounds with oxygen are called fluorides such as oxygen difluoride, OF_2 . On the other hand, oxygen is more electronegative than chlorine, bromine or iodine, so oxygen derivatives are called oxides such as chlorine dioxide, ClO_2 .

3.5.15.1 Some Important Points of Halides

1. All the elements form hexafluorides, i.e. fluorine brings out maximum valency of six with these elements due to its small size and highest electronegativity as compared to that of the atoms of the other halogens.
2. With the increase in the size of the halogen atom the maximum coordination number of the elements of group 16 decreases. Thus there are no hexachlorides.
3. Te_2Cl_2 and Po_2Cl_2 are not known because the bond between the two atoms such as Te-Te or Po-Po will be weaker due to their large size. Moreover, chlorine being highly electronegative, will withdraw electrons making Te-Te or Po-Po bond still more weak.
4. Generally, the order of thermal stability of the halides of any particular oxidation state decreases in the order:
 $\text{F} > \text{Cl} > \text{Br} > \text{I}$

3.5.16 HEXAHALIDES

Only fluorine forms hexafluorides, i.e. fluorine brings out the maximum valency of six with S, Se and Te. SF_6 , SeF_6 and TeF_6 are all formed by direct combination with fluorine, e.g.

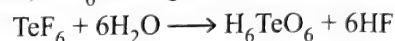


All the hexafluorides have octahedral structures, with the central atom (S, Se or Te) being sp^3d^2 hybridised (Figure 3.8)

SF_6 is a colourless, odourless and non-toxic gas at room temperature. It is thermally stable and chemically inert. Its chemical inertness is due to the reason that the six F atoms protect the sulphur atom from attack by the reagents to such an extent that even thermodynamically most favourable reactions like hydrolysis do not occur. However, as the size of the central atom increases, steric hindrance decreases and hence the hydrolysis becomes easy.

Alternatively, as the size of the atom increases, the electronegativity decreases and the bond polarities increase leading to increase in reactivity or decrease in stability down the group. Thus, the order of hydrolysis of hexafluorides is $\text{SF}_6 > \text{SeF}_6 > \text{TeF}_6$.

In other words, TeF_6 undergoes hydrolysis readily.



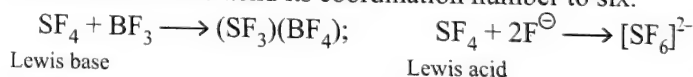
Similarly, TeF_6 adds F^- to form $[\text{TeF}_7]^-$ and $[\text{TeF}_8]^{2-}$ ions. Moreover, TeF_6 reacts with other Lewis bases such as amines to give eight coordinate adducts like $[(\text{CH}_3)_3\text{N}]_2\text{TeF}_6$.

All these hexafluorides are colourless gases, which means that they have very low boiling points which indicates a high degree of covalency.

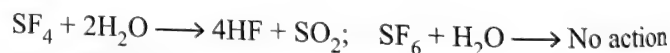
3.5.17 TETRAHALIDES

Many tetrahalides are known: SF_4 is a gas, SeF_4 is a liquid while TeF_4 is a solid. S, Se, Te and Po form tetrachlorides and bromides while Te and Po form tetraiodides. In all tetrahalides the central atom is sp^3d hybridised with 1 lp and hence possesses trigonal bipyramidal geometry in which one of the equatorial position is occupied by lone pair of electron. This lone pair repels the axial bond pairs thereby decreasing the bond angle from 180° to 173° in SF_4 . Thus SF_4 has see-saw shape.

The tetrahalides can act both as Lewis bases due to the presence of a lone pair of electrons and Lewis acids because the central atom can extend its coordination number to six.



Further, unlike SF_6 which does not undergo hydrolysis because the six F atoms protect the sulphur atom from attack by water due to steric hindrance. SF_4 readily undergoes hydrolysis because the four F atoms cannot protect the S atom from attack by water.



SF_4 readily undergoes hydrolysis due to the presence of vacant $3d$ orbitals in S, S can expand its coordination number. It is used as a fluorinating agent for many inorganic and organic compounds. Just like tetrafluorides, tetrachlorides especially TeCl_4 react with HCl to form complex ions such as $[\text{TeCl}_6]^{2-}$.

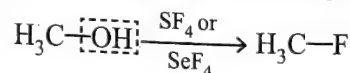
The stability of the tetrahalides increases with increase in polarity of the bonds, i.e., $\text{SCl}_4 < \text{SeCl}_4 < \text{TeCl}_4$.

Similarly, the stability of tetrabromides increases from SeBr_4 to PoBr_4 .

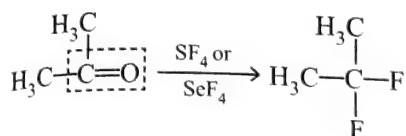
3.5.18 SF_4 AND SeF_4 AS FLUORINATING AGENTS

Both SF_4 and SeF_4 are used as fluorinating agents for the conversion of following groups e.g.,

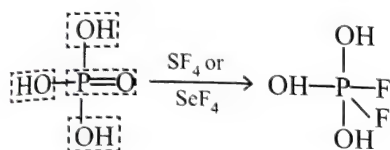
- i. (R-OH) group to (R-F) group. For example



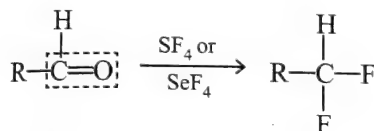
ii. $\left(\begin{array}{c} | \\ -\text{C}=\text{O} \\ | \end{array}\right)$ group to $\left(\begin{array}{c} | \\ -\text{C}-\text{F} \\ | \\ \text{F} \end{array}\right)$ group. For example



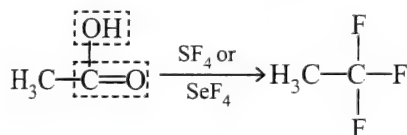
iii. $\left(\begin{array}{c} | \\ -\text{P}=\text{O} \\ | \end{array}\right)$ group to $\left(\begin{array}{c} | \\ -\text{P}-\text{F} \\ | \\ \text{F} \end{array}\right)$ group. For example



iv. $\left(\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{O} \end{array}\right)$ group to $\left(\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{F} \\ | \\ \text{F} \end{array}\right)$ group. For example



v. $\left(\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{OH} \end{array}\right)$ group to $\left(\begin{array}{c} \text{F} \\ | \\ -\text{C}-\text{F} \\ | \\ \text{F} \end{array}\right)$ group. For example



3.5.19 DIHALIDES

All the elements of group 16 except selenium form stable dichlorides and dibromides. Di-iodides are not formed. Dihalides form tetrahedral molecules due to sp^3 hybridisation of central atom. However, due to the presence of two lone pairs of electrons, they have bent structure like water.

In SCl_2 , the bond angle is little smaller (103°) as compared to that in H_2O (104.5°). This is due to the reason that S is less electronegative than O. As a result, the bond pairs of the two S-Cl bonds lie away from the S atom in SCl_2 as compared to those of O-H bonds in H_2O . Consequently, bond pair-bond pair repulsions decrease and hence the bond angle decreases to 103° in SCl_2 from 104.5° in H_2O .

3.5.20 MONOCHLORIDES

Dimeric monochlorides such as S_2F_2 , S_2Cl_2 and S_2Br_2 are known. Their structure is similar to H_2O_2 .

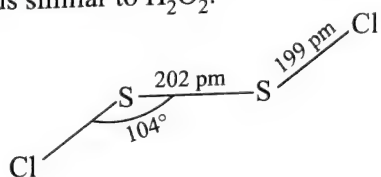


ILLUSTRATION 3.2

- Elements of group 16 generally show lower value of first ionisation enthalpy as compared to the corresponding periods of group 15. Why?
- H_2S is less than acidic than H_2Te . Why?

Sol.

- Elements of group 16 generally show lower value of first ionisation enthalpy as compared to the corresponding elements of group 15. This is due to the extra stability of half-filled electronic configuration of group 15 elements (ns^2np^3), hence more energy is required to remove an electron as compared to those of group 16 elements (ns^2np^4).
- Down the group (\downarrow), as the size of the element increases, E—H bond length increases and hence E—H bond strength decreases and bond dissociation energy decreases. In other words, H—S bond dissociation energy is more than that of H—Te bond dissociation energy and hence H—S bond ionises less readily than H—Te bond. Therefore, H_2S is a weaker acid than H_2Te .

3.6 ANOMALOUS BEHAVIOUR OF OXYGEN

Oxygen the first member of group 16 differs from the rest of member due to (a) small size, (b) high EN and (c) non-availability of d -orbitals in the valence shell.

The main points of difference between oxygen and the rest of the members of group 16 are as follows:

- Physical state:** Oxygen is a gas at room temperature while other members are solids.
- Atomicity:** Oxygen molecule is diatomic (O_2) while the molecules of the other elements are more complex, e.g., sulphur and selenium have octa-atomic molecules (i.e., S_8 and Se_8) with puckered ring structures.
- Non-metallic/metallic character:** Being highly electronegative (3.5), oxygen is a typical non-metal. Sulphur (EN = 2.5) is also non-metallic but other members of this group exhibit metallic character also.
- Oxidation states:** Being most electronegative element of the group, oxygen usually shows an oxidation state of -2 in most of its compounds (except in peroxides, O_2F_2 and OF_2). Sulphur also shows an oxidation state of -2 to some extent. Other elements of this group, however, do not show negative oxidation states. Further, oxygen does not have d -orbitals. That is why it cannot expand its octet and hence cannot show positive oxidation states. However, other elements of this group have vacant d -orbitals in the valence shell and hence can show positive oxidation states of $+2$, $+4$ and $+6$.
- Nature of compounds:** Due to high electronegativity, oxygen is more ionic in its compounds. The dinegative anion (O^{2-}) is very common. The dinegative anions of other

elements (i.e., S^{2-} , Se^{2-} , Te^{2-}) are less common. In other words, compounds of oxygen are ionic as well as covalent while those of sulphur and other members of this group are mostly covalent.

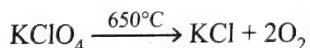
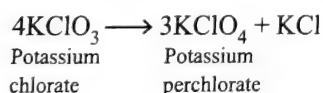
6. **Multiple bonds:** Due to small size and high electronegativity, oxygen forms $p\pi-p\pi$ multiple bonds with elements having similar size, i.e., carbon, nitrogen ($C=O$, $C=N$, $C\equiv N$), etc. This tendency of forming multiple bonds is not shown by other elements of this group mainly due to larger size and lower electronegativity.
7. **Hydrogen bonding:** Due to high electronegativity, oxygen forms H-bonds. For example, the hydride of oxygen (H_2O) forms intermolecular H-bonds while hydrides of other elements of this group (H_2S , H_2Se , etc.) do not. As a result, H_2O is a liquid at room temperature while hydrides of other elements are gases.
8. **Magnetic nature:** Due to the presence of two unpaired electrons, O_2 is paramagnetic in gaseous, liquid and solid states. The other elements of this group are however, diamagnetic.

3.7 DIOXYGEN

Priestley and Scheele obtained oxygen by heating suitable oxygen compounds. Scheele called it **vital air** or **fire air**. Lavoisier regarded it as an **essential constituent** of all acids and named it **oxygen** (oxus = acid, gennas = maker).

3.7.1 LABORATORY PREPARATION

The usual laboratory method is of heating a mixture of potassium chlorate and manganese dioxide in the ratio of 4 : 1. $KClO_3$ evolves oxygen at $375^\circ C$. At this temperature, it melts and gets converted into potassium perchlorate which decomposes at higher temperature to evolve oxygen. When MnO_2 is added, it starts giving oxygen at $250^\circ C$. Here MnO_2 acts as a catalyst.



MnO_2 used for this purpose should be completely free from carbon as $KClO_3$ and carbon mixture is explosive in nature. The mixture should be first heated gently and then strongly when it is ensured that there is no vigorous reaction.

3.7.2 COMMERCIAL METHODS

The main sources for large-scale preparation of dioxygen are air and water.

From liquid air: The most economical method for commercial preparation of dioxygen involves liquefaction of air (after removing CO_2 and water vapours) followed by fractional distillation of the liquid air thus obtained. During this process, dinitrogen (N_2) with lower boiling point (77 K) distils over in the gaseous form leaving behind dioxygen with higher boiling point (90 K) in the liquid state.

3.8 PHYSICAL AND CHEMICAL PROPERTIES OF OXYGEN

3.8.1 Physical Properties

1. a. Oxygen is a colourless, odourless and tasteless gas.
b. Liquid dioxygen is pale blue in colour, and the solid is also blue. The colour arises due to electronic transitions which excite the ground state (triplet state) to a singlet state. This transition is forbidden in gaseous dioxygen. In liquid or solid O_2 , a single photon may collide with two molecules simultaneously and promote both the molecules to excited states, absorbing red-yellow-green light, so O_2 appears blue.

Second excited state (electrons have opposite spins) $\pi^*p_y \pi^*p_z$

1	↓
---	---

 Singlet

First excited state (electrons are paired)

↑↓

 Singlet

Ground state (electrons have parallel spins)

1	1
---	---

 Triplet

2. Liquefies at 90 K and freezes at 55 K.
3. Despite having even number of electrons, oxygen is paramagnetic. This can be explained on the basis of molecular orbital diagram for O_2 molecule (Figure 2.78 (Part 1)).

3.8.2 Chemical Properties

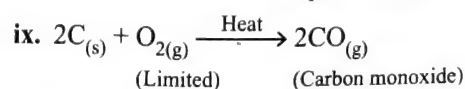
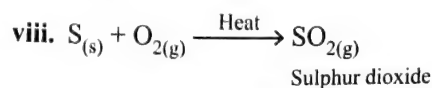
The bond dissociation energy of dioxygen is high ($493.4 \text{ kJ mol}^{-1}$) and hence the reactions of dioxygen require initiation by external heating. However, when the reaction starts, it continues on its own. This is due to the reason that the chemical reactions of dioxygen are exothermic and the heat liberated during the reaction is sufficient to carry on the reactions.

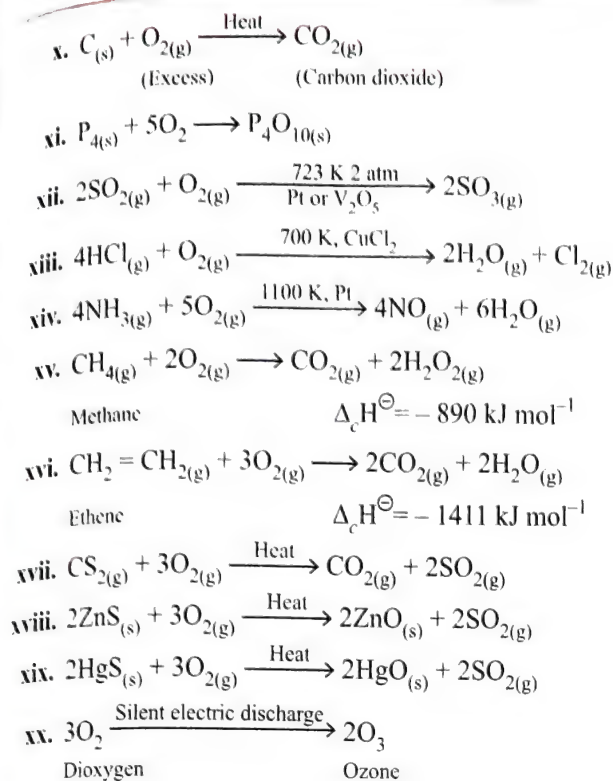
3.8.2.1 Some Important Chemical Properties

Reactions of Oxygen

- i. $4Na_{(s)} + O_{2(g)} \longrightarrow 2Na_2O_{(s)}$
- ii. $2Na_{(s)} + O_{2(g)} \xrightarrow{575 \text{ K}} Na_2O_{2(s)}$
- iii. $2Mg_{(s)} + O_{2(g)} \xrightarrow{\text{Heat}} 2MgO_{(s)}$
- iv. $4Al_{(s)} + 3O_{2(g)} \xrightarrow{\text{Heat}} 2Al_2O_{3(s)}$
- v. $4Fe_{(s)} + 3O_{2(g)} \xrightarrow{\text{Heat}} 2Fe_2O_{3(s)}$
- vi. $2H_{2(g)} + O_{2(g)} \xrightarrow[1073 \text{ K or Electric discharge}]{} 2H_2O_{(g)}$
- vii. $N_{2(g)} + O_{2(g)} \xrightarrow{3300 \text{ K}} 2NO_{(g)}$

This reaction occurs in the atmosphere, when lightning occurs in the sky.



**Uses:**

1. Liquid oxygen is an important constituent of fuels used in rockets.
2. Oxygen is used for production of oxyhydrogen or oxyacetylene flames which are employed for cutting and welding purposes.
3. Oxygen mixed with helium or carbon dioxide is used for artificial respiration.
4. Oxygen is used in the manufacture of large number of compounds such as phenol, ethylene oxide, sulphur dioxide, sulphuric acid, nitric acid, chlorine, etc.
5. Liquid oxygen mixed with finely divided carbon acts like a dynamite in coal mining.
6. Oxygen is used as an oxidising agent in several reactions.
7. ^{18}O is used as a tracer in the study of tracer mechanisms.

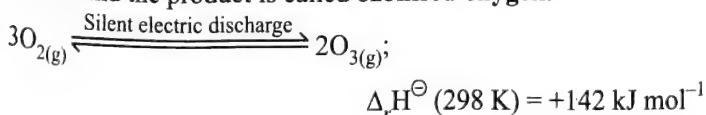
3.9 OZONE OR TRIOXYGEN (O_3)

3.9.1 INTRODUCTION

In 1758, **Van Marum** observed a rotten smell when an electric discharge was passed through air. In 1840, **Schonbien** attributed that the rotten smell was due to formation of a new gas which he named ozone. The name ozone comes from the Greek word *ozo* meaning *smell*. In 1866, **Sorret** established its formula, O_3 , and pointed out that the ozone is an allotrope of oxygen.

3.9.2 PREPARATION

Ozone is prepared by passing a silent electric discharge through pure, cold and dry dioxygen in a specially designed apparatus called the **ozoniser**. During this reaction, conversion of O_2 to ozone is 10% and the product is called **ozonised oxygen**.



Since the formation of ozone from oxygen is endothermic process, hence it is necessary to use a silent electric discharge (sparkless electric discharge) in its preparation. A silent electric discharge produces less heat and thus prevents the decomposition of ozone back to oxygen.

If concentration of ozone greater than 10% is required, a battery of ozonisers is used and the pure ozone (b.p. 161 K) can be condensed in a vessel surrounded by liquid oxygen.

3.9.3 STRUCTURE OF OZONE

The central oxygen atom in ozone is sp^2 -hybridised containing a lone pair of electrons. As a result, ozone has an angular structure with a bond angle of 117° as shown in Figure 3.7.



Fig. 3.7 Structure of ozone

It is actually a resonance hybrid of the following two resonating structures (I and II) as shown in figure 3.8.

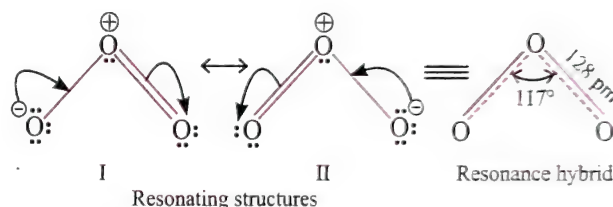


Fig. 3.8 Resonance structure of ozone

Because of resonance, both the oxygen—oxygen bonds have partial double bond character. In other words, both the oxygen—oxygen bonds are equal (128 pm) and lie in between those of oxygen—oxygen double bond length of 110 pm and oxygen—oxygen single bond length of 148 pm.

3.9.4 PHYSICAL PROPERTIES

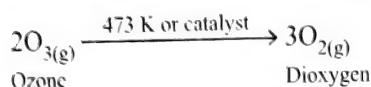
1. When cooled in liquid air, pure ozone condenses to a deep blue liquid (boiling point 161 K) and then to a violet-black solid (melting point 80 K).
2. It is about 1.67 times heavier than air because its vapour density (V.D.) is 24 while that of air is 14.4.
3. Ozone is a pale blue gas having a strong characteristic smell. In small concentration, it is harmless. However, if the concentration rises above 100 parts per million (ppm), breathing becomes uncomfortable resulting in headache and nausea.
4. It is slightly soluble in water but readily dissolves in organic solvents such as turpentine oil, cinnamon oil, carbon tetrachloride, glacial acetic acid, etc.
5. Ozone is diamagnetic while dioxygen is paramagnetic.

3.9.5 CHEMICAL PROPERTIES

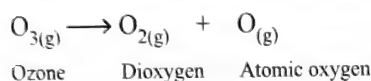
1. **Neutral character:** Ozone is neutral to litmus.
2. **Decomposition:** Ozone is thermodynamically unstable as compared to oxygen since its decomposition into oxygen

results in liberation of heat (ΔH is $-ve$) and an increase in entropy (ΔS is $+ve$). These two factors reinforce each other, resulting in large negative Gibbs free energy change (ΔG) for the decomposition of ozone to oxygen. Therefore, high concentration of ozone can be dangerously explosive.

Even at ordinary temperature, it decomposes slowly to give oxygen. However, when heated to 473 K or in presence of a catalyst such as manganese dioxide, platinum or cupric oxide, the decomposition takes place rapidly.

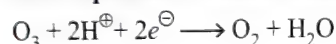


3. **Oxidising:** Ozone is a powerful oxidising agent, second only to F_2 but much stronger than dioxygen. This is due to the reason that ozone has higher energy content than dioxygen and hence decomposes to give dioxygen and atomic oxygen.

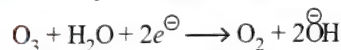


The atomic oxygen thus liberated brings about the oxidation while molecular oxygen is set free.

Ionic equation in acidic medium:

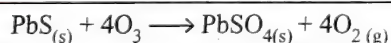
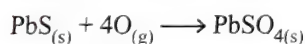
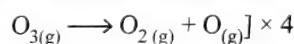


Ionic equation in basic medium:



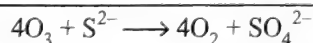
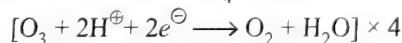
Some important reactions of O_3 are

- a. It oxidises (PbS to white PbSO_4) and also sulphides of Cu, Zn and Cd to their respective sulphates

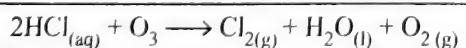
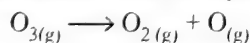


Ionic equation:

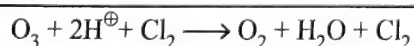
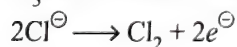
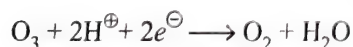
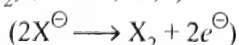
It oxidises ($\text{S}^{2-} \longrightarrow \text{SO}_4^{2-} + 8e^{\ominus}$)



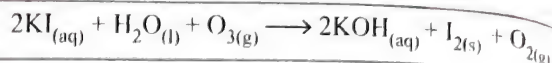
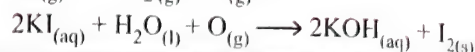
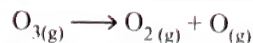
- b. It oxidises HX to corresponding X_2



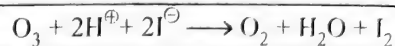
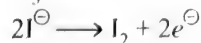
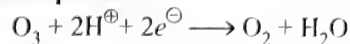
Ionic equation: It oxidises (X^{\ominus} to X_2) ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)



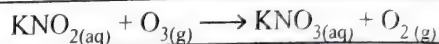
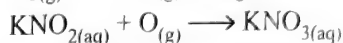
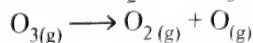
- c. It oxidises moist KI to I_2 ($\text{I}^{\ominus} \longrightarrow \text{I}_2$)



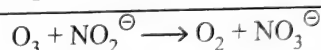
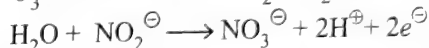
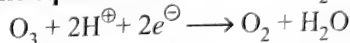
Ionic equation:



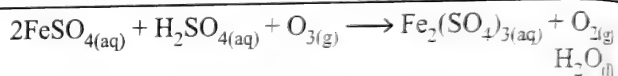
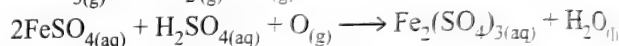
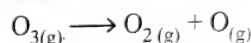
- d. It oxidises NO_2^{\ominus} to NO_3^{\ominus}



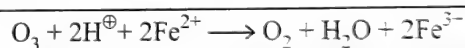
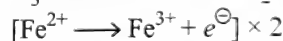
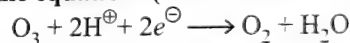
Ionic equation: It oxidises ($\text{NO}_2^{\ominus} \longrightarrow \text{NO}_3^{\ominus} + 2e^{\ominus}$)



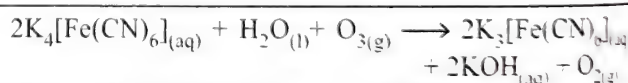
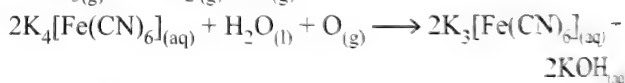
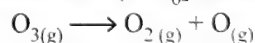
- e. It oxidises Fe^{2+} salts to Fe^{3+} salts



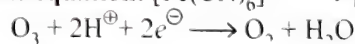
Ionic equation: ($\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^{\ominus}$)



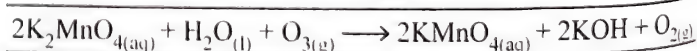
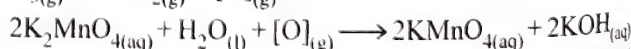
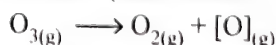
- f. It oxidises $\text{Fe}(\text{CN})_6^{4-}$ salts to $\text{Fe}(\text{CN})_6^{3-}$ salts



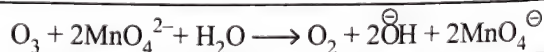
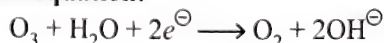
Ionic equation: $[\text{Fe}(\text{CN})_6]^{4-} \longrightarrow [\text{Fe}(\text{CN})_6]^{3-} + e^{\ominus}$



- g. It oxidises MnO_4^{\ominus} (green) to MnO_4^{2-} (pink-violet) in basic medium (used as test for ozone)



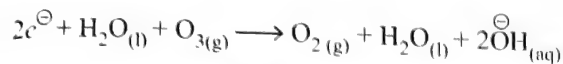
Ionic equation:



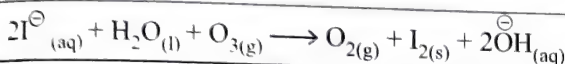
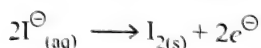
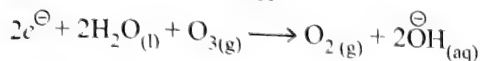
3.9.6 QUANTITATIVE ESTIMATION OF O₃

When O₃ reacts with an excess of KI solution buffered with a borate buffer (pH = 9.2), I₂ is liberated which can be titrated against a standard solution of Na₂S₂O₃ (sodium thiosulphate). This is a quantitative method of estimation of O₃ gas.

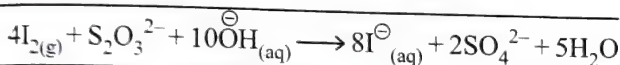
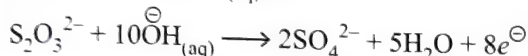
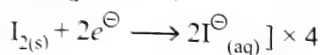
1. Ionic equation of O₃ and I[−] ion in basic medium (pH = 9.2) is



OR



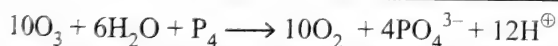
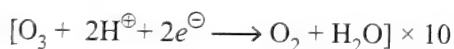
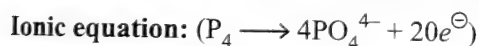
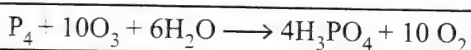
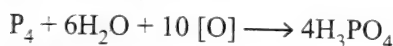
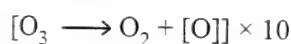
2. Ionic equation of liberated I₂ with standard Na₂S₂O₃ in basic medium (pH = 9.2)



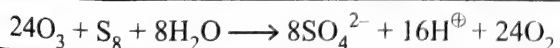
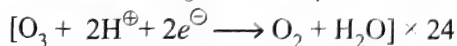
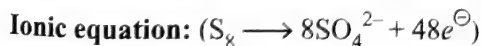
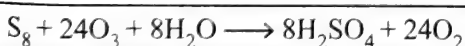
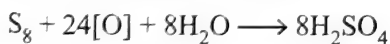
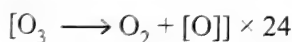
3.9.7 OXIDATION OF NON-METALS

Ozone oxidises non-metals like phosphorous, sulphur and iodine to their corresponding oxyacids. For example,

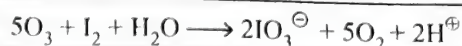
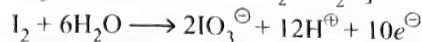
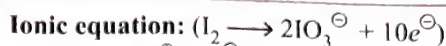
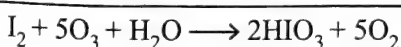
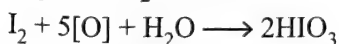
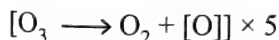
1. It oxidises moist phosphorous to phosphoric acid or phosphate ion



2. It oxidises moist sulphur to sulphuric acid or sulphate ion

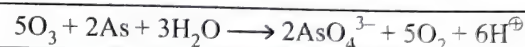
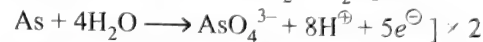
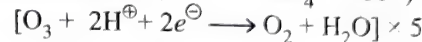
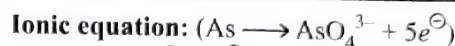
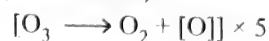


3. It oxidises moist iodine to iodic acid or iodate ion



3.9.8 OXIDATION OF METALLOIDS

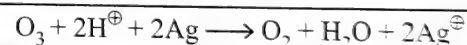
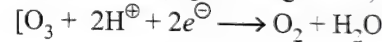
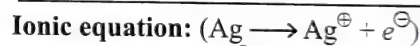
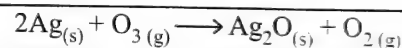
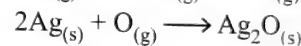
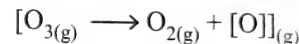
Ozone also oxidises metalloids like As to its corresponding oxyacid. (arsenate ion)



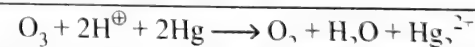
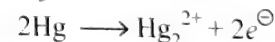
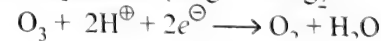
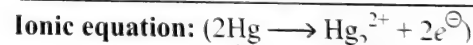
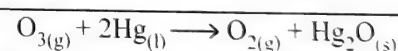
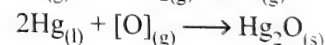
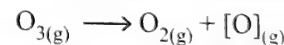
3.9.9 OXIDATION OF METALS

Ozone also oxidises certain metals like silver, mercury, copper, etc. to their corresponding oxides. For example,

1. Silver is oxidised to silver oxide (Ag₂O)

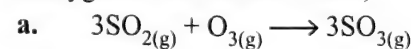


2. Mercury is oxidised to mercurous oxide (Hg₂O)



The mercurous oxide thus formed dissolves in mercury which loses its meniscus and starts sticking to the glass. This is called **tailing of mercury**. The meniscus can, however, be restored by shaking it with water which dissolves mercurous oxide. This reaction is used as a test of ozone.

3. **Exceptional behaviour:** In all the oxidation reactions discussed above, the oxidation is brought about by the atomic oxygen and dioxygen is always evolved. However during the oxidation of SO₂ to SO₃ and SnCl₂ in presence of conc. HCl to SnCl₄ the ozone is utilised as a whole and dioxygen is not evolved. Thus,



Sulphur dioxide

Sulphur trioxide

2. Different chain polymers known as catena S_n sulphur.

The most important allotrope of this category is **plastic sulphur** or γ -sulphur.

Preparation: It is obtained by pouring molten sulphur into cold water when a soft rubber like mass called plastic sulphur is obtained.

Properties:

- It does not have a sharp melting point.
- It is an amorphous form of sulphur. It is soft and elastic like rubber in the beginning but hardens on standing and cooling and gradually changes into rhombic sulphur.
- It has rubber like transparent yellow threads and is insoluble in CS_2 and H_2O .
- Its specific gravity is 1.95 g cm^{-3} .

Plastic sulphur is regarded as a super-cooled liquid, i.e., a liquid which because of rapid cooling below its melting point has no time to settle in a crystalline form.

Structure:

Plastic sulphur consists of zig-zag chains (Figure 3.10) and sometimes S_8 and other rings.

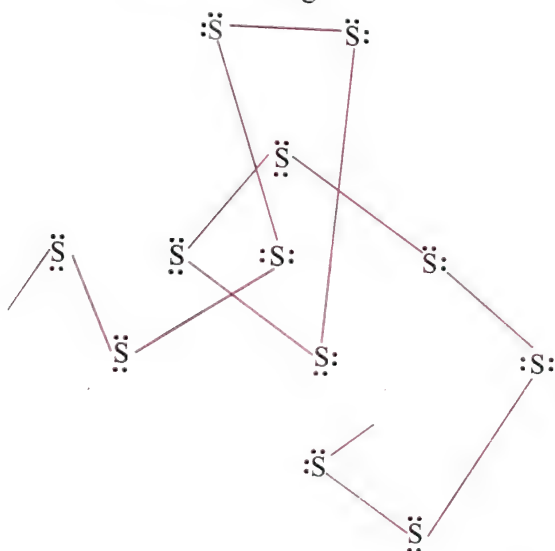
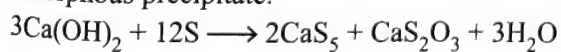


Fig. 3.10 Zig-zag chains of sulphur atoms in plastic sulphur

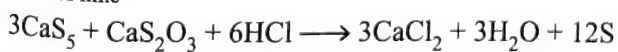
- Unstable small molecules S_n ($n = 2-5$):** These molecules exist in different concentrations in liquid sulphur at higher temperatures and in sulphur vapours. S_2 species predominate at about 1000 K. Like dioxygen (O_2), S_2 is paramagnetic and blue coloured and presumably has similar bonding.

4. Preparation of milk of sulphur:

It is obtained by boiling milk of lime with sulphur and decomposing the calcium pentasulphide thus formed with HCl , when milk of sulphur is precipitated as white amorphous precipitate.



Milk of lime



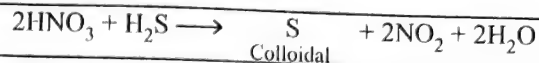
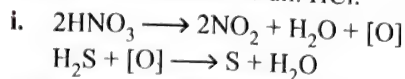
Milk of sulphur

Properties: Milk of sulphur is soluble in CS_2 and is largely used in medicine.

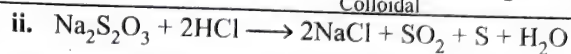
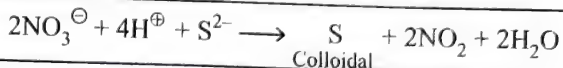
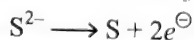
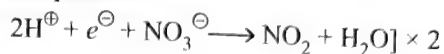
5. Preparation of colloidal of δ -sulphur:

Sulphur is precipitated in the colloidal form when hydrogen

sulphide is bubbled through nitric acid or when $Na_2S_2O_3$ solution is treated with dil. HCl .



Ionic equation:

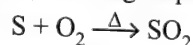


Property: On heating or long standing, colloidal sulphur changes into the ordinary form.

3.11 SULPHUR DIOXIDE (SO_2)

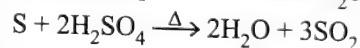
Preparation:

- By burning sulphur in air or oxygen

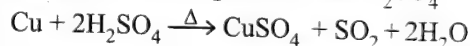


- In laboratory, SO_2 can be prepared by

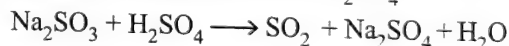
- Heating sulphur with conc. H_2SO_4



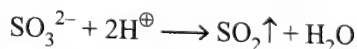
- Heating Cu turnings with conc. H_2SO_4



- Treating a sulphite with dil. H_2SO_4

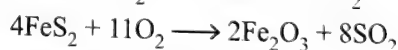
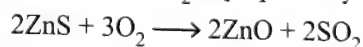


or

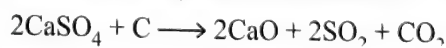


The gas dried, liquefied under pressure and stored in steel cylinders.

- In industry, SO_2 is prepared by roasting of sulphides.



- In places, where gypsum or anhydrite ore is found in abundance, SO_2 can be obtained on a large scale by heating gypsum or anhydrite with carbon at $\sim 1000^\circ\text{C}$



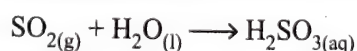
Properties:

Physical properties:

- It is heavier than air.
- It is highly soluble in water.
- It can be easily liquefied to a colourless liquid at -10°C and into a snowlike solid at -76°C .
- It is a colourless gas with a pungent, suffocating odour.

Chemical properties:

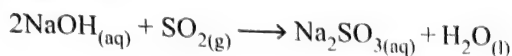
- Acidic nature:** Sulphur dioxide dissolves in water to form sulphurous acid, and thus acts as an acidic oxide.



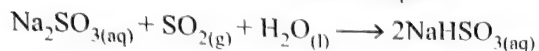
Therefore, SO_2 is regarded as anhydride of sulphurous acid.

Its aqueous solution is acidic and turns blue litmus red. SO_2 , being acidic undergoes the following reactions:

- a. It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium bisulphite (sodium hydrogen sulphite).

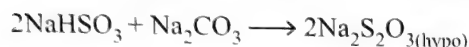
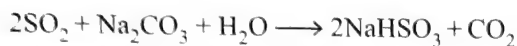
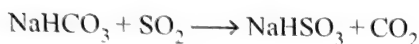


Sodium sulphite

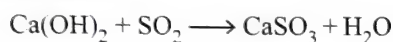


Sodium bisulphite

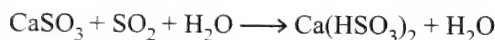
- b. It also decomposes carbonates and bicarbonates evolving CO_2 gas.



- c. **Action on lime water:** Like CO_2 , it turns lime water milky due to the formation of insoluble calcium sulphite. However, if SO_2 is passed for a long time, milkiness disappears due to the formation of soluble sodium bisulphite.

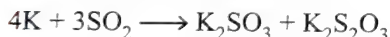


(Milkiness)



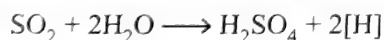
Calcium bisulphite (soluble)

2. **Non-supporter of combustion:** SO_2 gas is neither combustible nor a supporter of combustion. However, certain substances like heated carbon, lighted magnesium ribbon or heated potassium metal continue to burn on heating.



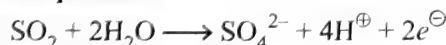
This is due to the reason that high heat of the reaction dissociates SO_2 to S and O_2 and the O_2 thus produced helps combustion.

3. **Reducing nature:** In presence of moisture, SO_2 acts as a good reducing agent. Its reducing character is due to the evolution of nascent hydrogen.



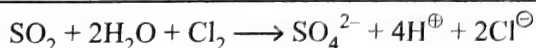
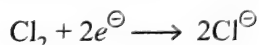
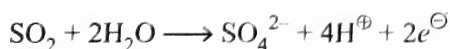
or

Ionic equation:



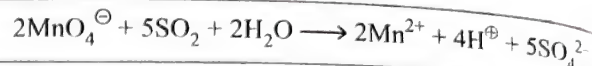
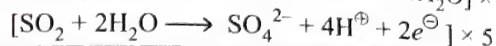
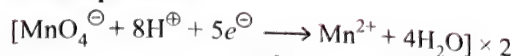
Few examples are as follows:

- a. Reduces halogens to halogen acids ($\text{X}_2 \longrightarrow \text{X}^-$)

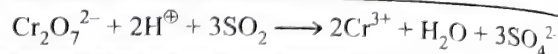
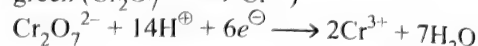


- b. It decolourises pink violet colour of acidified KMnO_4 solution, as SO_2 reduces MnO_4^- to Mn^{2+}

Ionic equation:



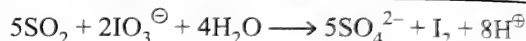
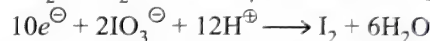
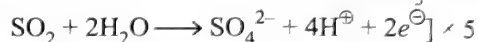
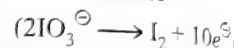
- c. It turns orange coloured potassium dichromate solution green ($\text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cr}^{3+}$)



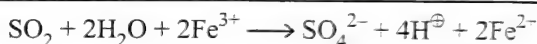
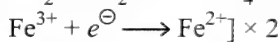
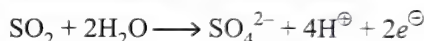
- d. It reduces lead dioxide to lead sulphate



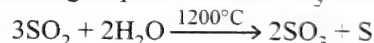
- e. It reduces acidified potassium iodate to iodine



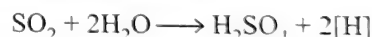
- f. It reduces ferric to ferrous salts



4. **Thermal decomposition:** SO_2 decomposes at 1200°C producing sulphur trioxide, SO_3 and sulphur.



5. **Bleaching action:** SO_2 is a mild bleaching agent. Its bleaching action is due to reduction of the vegetable colouring matter by nascent hydrogen liberated in the presence of moisture.



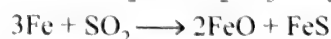
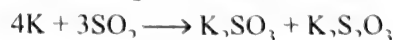
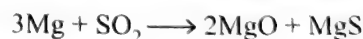
Vegetable colouring matter + $[\text{H}] \longrightarrow$ colourless vegetable matter.

Bleaching by SO_2 is, however, **temporary**. When the bleached article is exposed to air, it regains its colour due to oxidation.

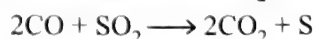
6. **Oxidising nature:** It acts as a mild oxidising agent particularly when it reacts with strong reducing agents.

- a. Oxidises H_2S to S: $2\text{H}_2\text{S} + \text{SO}_2 \longrightarrow 2\text{H}_2\text{O} + 3\text{S}$

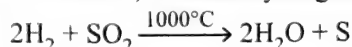
- b. Active metals are oxidised:



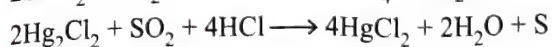
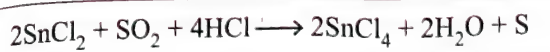
- c. CO is oxidised to CO_2 :



- d. At 1000°C , oxidises hydrogen into water

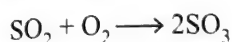


- e. In presence of excess of HCl, stannous and mercurous salts are oxidised

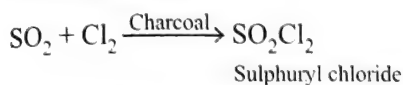


7. Addition reactions:

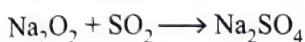
- a. It combines with O_2 in presence of platinised asbestos at 723 K or in presence of V_2O_5 at 773 K to form sulphur trioxide



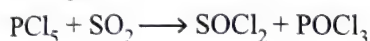
- b. It reacts with Cl_2 in presence of charcoal as catalyst to form sulphuryl chloride



- c. It combines with sodium peroxide to form sodium sulphate, Na_2SO_4 .



8. With PCl_5 , it gives thionyl chloride, SOCl_2 .



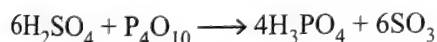
Uses:

- In the refining of petroleum and bleaching of sugarcane juice.
- As a bleaching agent for delicate articles like wool, silk and straw.
- In the manufacture of sulphuric acid, calcium hydrogen sulphite and sodium metabisulphite which is used as a preservative for jams, jellies and squashes.
- As a disinfectant for killing germs, fungi and certain moulds.
- As a solvent to dissolve a number of organic and inorganic chemicals.
- As an antichlor for removing excess of Cl_2 from a fabric after bleaching.
- Liquid SO_2 is used as a refrigerant.

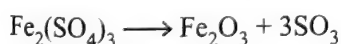
3.12 SULPHUR TRIOXIDE (SO_3)

Preparation:

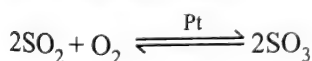
- By dehydrating sulphuric acid with excess of phosphorus pentoxide.



- By heating ferric sulphate strongly.



- By oxidation of SO_2 with oxygen in presence of a catalyst (commercial method).



Both SO_2 and O_2 should be completely dry. The mixture is passed over platinised asbestos at 400°C , when SO_3 is formed.

Properties:

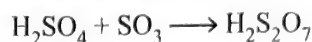
- SO_3 exists in three allotropic forms:

- a. $\alpha\text{-SO}_3$: It is a chemically active form. It forms long transparent ice like crystals. The melting point of this form is 17°C .

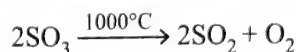
- b. $\beta\text{-SO}_3$: It is a dimeric form (S_2O_6). It forms needle-like silky white crystals. It melts at 32.5°C . Above 50°C , it changes to α -form.

- c. $\gamma\text{-SO}_3$: It is like β -form and obtained by completely drying $\beta\text{-SO}_3$. It melts at 62.2°C under 2 atmospheric pressure.

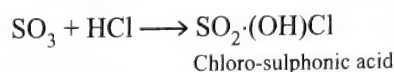
- It dissolves in concentrated sulphuric acid forming oleum (fuming sulphuric acid).



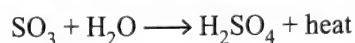
- It dissociates on heating at 1000°C into SO_2 and O_2 .



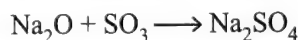
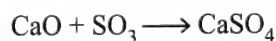
- It combines with concentrated hydrochloric acid and forms chloro-sulphonic acid, a derivative of sulphuric acid.



- SO_3 is an acidic oxide. It dissolves in water forming sulphuric acid with evolution of heat.

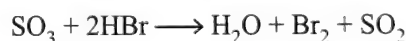
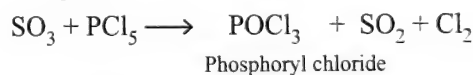
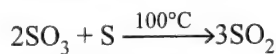


It reacts with basic oxides forming sulphates.



- SO_3 acts as an oxidising agent.

Examples:



Uses:

- In the manufacture of sulphuric acid and oleum.
- It is used as a drying agent for gases.

ILLUSTRATION 3.3

- Which form of sulphur shows paramagnetic behaviour?
- Compounds of fluorine and oxygen are called fluorides and not oxides. Explain.
- Sulphur disappears when boiled with an aqueous solution of sodium sulphite. Why?

Sol.

- In vapour state, sulphur partly exists as S_2 molecules and S_8 molecule like O_2 molecule has two unpaired electrons in the antibonding π^* -orbitals and exhibits paramagnetic nature.
- This is because of higher electronegativity of fluorine than oxygen. In naming a compound, the electropositive or less electronegative element is taken first, thus, the compounds of fluorine and oxygen are called oxygen fluorides and fluorine oxides.
- Sulphur combines with sodium sulphite and forms sodium thiosulphate which is soluble in water and hence S disappears.

ILLUSTRATION 3.4

Knowing the electron gain enthalpy values for $O \rightarrow O^{\ominus}$ and $O \rightarrow O^{2-}$ as -141 kJ mol^{-1} and $+702 \text{ kJ mol}^{-1}$ respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^{\ominus} ?

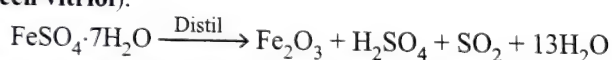
Sol. Although the formation of O^{2-} anion requires more energy in comparison to the formation of O^{\ominus} anion (actually energy is released), yet in large number of oxides, oxygen is divalent in nature. This is due to the fact that lattice energies of the oxides having O^{2-} anions are very high on account of greater magnitude of electrostatic forces of attraction.

3.13 OXOACIDS OF SULPHUR

A large number of oxyacids are known in the case of sulphur either in free state or in the form of salts or both. Oxyacids with S-S links are called thioacids. Acids having sulphur in lower oxidation state belong to -ous series while those having sulphur in higher oxidation state belong to -ic series. The name, formula, structure, O.S. and properties of some oxo-acids of sulphur are given in Table 3.2.

3.14 SULPHURIC ACID (H_2SO_4)

Sulphuric acid, in ancient days, was called **oil of vitriol** as it was prepared by distilling ferrous sulphate, $FeSO_4 \cdot 7H_2O$ (also known as **green vitriol**).



Sulphuric acid is considered as **king of chemicals**. The prosperity of any country is measured by the amount of H_2SO_4 it consumes. H_2SO_4 is a chemical of great commercial importance as it is used practically in every important industry.

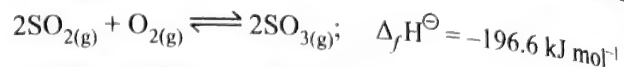
3.14.1 MANUFACTURE OF H_2SO_4 BY CONTACT PROCESS

Sulphuric acid is manufactured these days by contact process (Figure 3.11) which involves the following steps:

1. Production of SO_2 by burning sulphur or sulphide ores, e.g. iron pyrites in air.

$$S_8 + 8O_2 \xrightarrow{\Delta} 8SO_2; \quad 4FeS_2 + 11O_2 \xrightarrow{\Delta} 2Fe_2O_3 + 8SO_2$$

(Air) Iron pyrites
2. Catalytic oxidation of sulphur dioxide by air to give sulphur trioxide.



This step is the key step in the manufacture of H_2SO_4 . In accordance with **Le Chatelier's** principle, the favourable conditions for the maximum yield of SO_3 are as follows:

- a. High pressure:** Since the forward reaction proceeds with decrease in number of moles, hence high pressure will favour the reaction. In actual practice, a pressure of about 2 bars is used. This is because gases are acidic and corrosion of the plant occurs at high pressures.
- b. Low temperature:** Since the forward reaction is exothermic, therefore, low temperature will favour the reaction. However, rate of the reaction decreases with decrease in temperature. Therefore, the reaction is carried out at an optimum temperature of 720 K.
- c. Use of a catalyst:** To increase the rate of reaction at low temperature, a catalyst e.g. V_2O_5 or Fe_2O_3 is used. Since platinum is costly and is easily poisoned by arsenic impurities usually present in SO_2 , therefore, these days, divanadium pentoxide V_2O_5 is used because it is cheaper as well as not easily poisoned.
- d. Purity of gases:** To prevent poisoning of catalyst, the gases must be free from the impurities of As_2O_3 dust particles and moisture.
- e. Excess of oxygen:** To have maximum yield of SO_3 , O_2 is used in excess.
- f. Absorption of sulphur trioxide in 98% sulphuric acid to form oleum.**

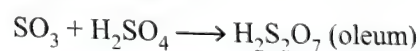
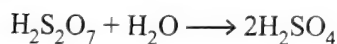


Table 3.2 Some Oxyacid of sulphur

Name of acid	Formula	O.S.	Structure	Property
Sulphurous acid series:				
a. Sulphurous acid	H_2SO_3	+4		Acts as oxidising and reducing agent
b. Thiosulphurous acid	$H_2S_2O_2$	+1		—
c. Hyposulphurous acid or Hydrosulphurous acid or Dithionous acid	$H_2S_2O_4$	+3		—
d. Di or pyrosulphurous acid	$H_2S_2O_5$	+4		—S—S—linkage, not known in free state

Sulphuric acid series:				
e. Sulphuric acid	H_2SO_4	+6		Acts as dehydrating, oxidising and pickling agent
f. Thiosulphuric acid	$\text{H}_2\text{S}_2\text{O}_3$	+6		—
g. Pyrosulphuric acid	$\text{H}_2\text{S}_2\text{O}_7$	+6		It is known as fuming sulphuric acid or anhydride of sulphuric acid or oleum
Thionic acid series:				
h. Dithionic acid	$\text{H}_2\text{S}_2\text{O}_6$	+5		—
i. Polythionic acid	$\text{H}_2\text{S}_n\text{O}_6$ ($n = 1$ to 6)	+5		—
Peroxy acid series:				
j. Peroxy monosulphuric acid (Caro's acid)	H_2SO_5	+6		-O-O-linkage
k. Peroxy disulphuric acid (Marshall's acid)	$\text{H}_2\text{S}_2\text{O}_8$	+6		-O-O-linkage
l. Sulphoxylic acid	H_2SO_2	+2	Not known	Not known in free state

g. **Dilution of oleum to get sulphuric acid of desired concentration.**



3. Absorption of SO_3 in H_2SO_4 to give oleum ($\text{H}_2\text{S}_2\text{O}_7$).

In industry, the two steps, i.e., absorption of SO_3 in H_2SO_4 to form oleum and its subsequent dilution with water are carried out simultaneously to make the process a continuous one and also to reduce the cost.

The sulphuric acid obtained by the contact process is 96–98% pure.

The plant consists of the following parts:

1. **Pyrite or sulphur burners:** Sulphur dioxide is produced by roasting pyrites or by burning sulphur in air.
2. **Purifying unit:** It consists of the following parts:
 - a. **Dust remover:** Dust is removed either by blowing steam or by using Cottrell electrical precipitator.
 - b. **Scrubber or washer:** Soluble impurities are removed by washing gases with water.

c. **Drier:** A spray of conc. H_2SO_4 is used for drying of gases.

d. **Arsenic purifier:** Gelatinous $\text{Fe}(\text{OH})_3$ is used to absorb impurities.

3. **Catalytic converter:** The pure gases coming from the testing box are preheated to 720 K in a preheater. The gases are then passed over a catalyst consisting either of platinised asbestos or V_2O_5 . Under these conditions, SO_2 gets oxidised to SO_3 and the heat produced in the reaction is used for heating the gases in the preheater.

4. **Absorption tower:** SO_3 from the catalytic converter is introduced at the base of the absorption tower from the top of which H_2SO_4 (98%) is showered. As SO_3 moves above, it is absorbed by H_2SO_4 forming oleum.

Oleum is then diluted with water to get H_2SO_4 of desired concentration.

It may be noted that sulphur trioxide is not directly absorbed in water to form sulphuric acid because it forms a dense fog of sulphuric acid which does not condense easily.

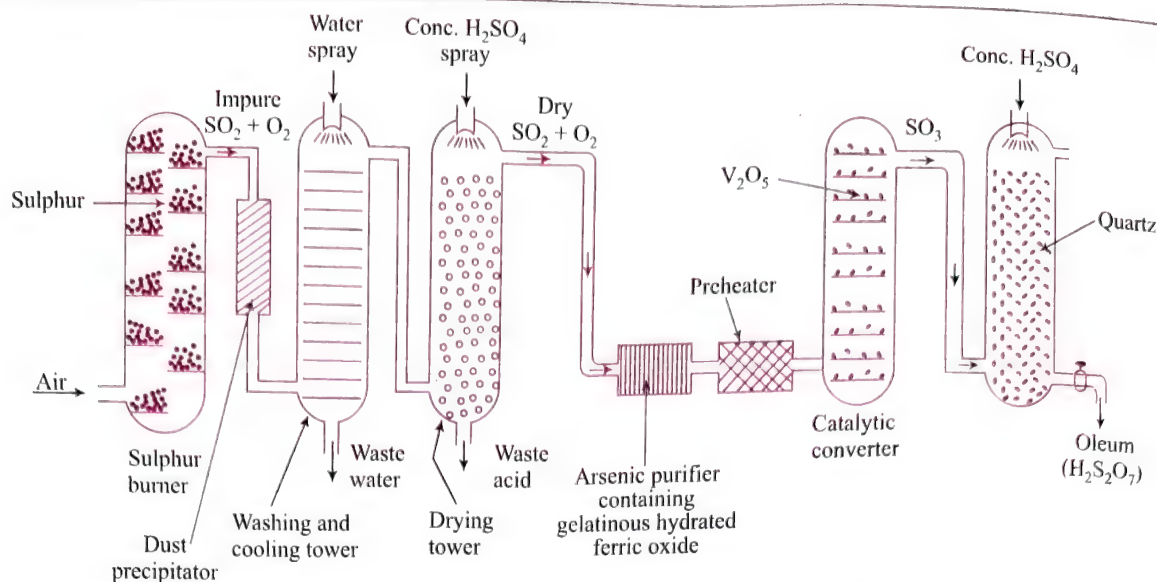
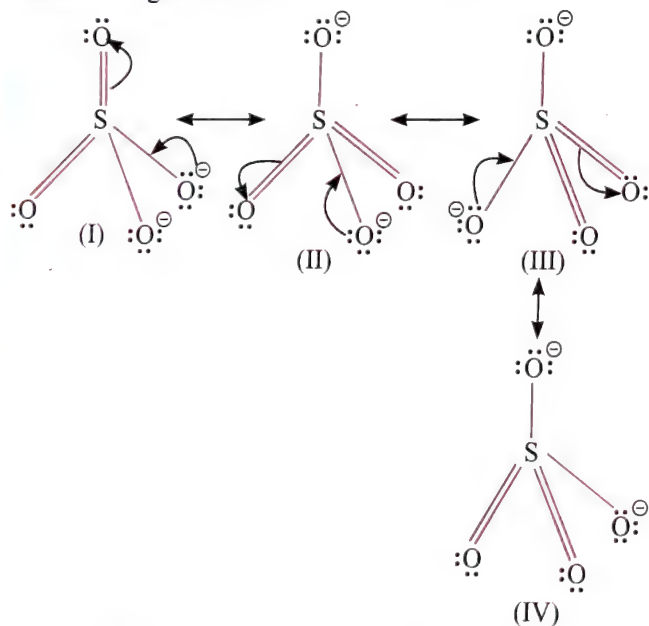


Fig. 3.11 Contact process for the manufacture of sulphuric acid

3.14.2 STRUCTURES

Both sulphuric acid and sulphate ion have tetrahedral structure in which sulphur is sp^3 -hybridised.

In sulphate ion, all the S–O bond lengths are equal, i.e. 149 pm. hence, it is a resonance hybrid of four structures (I, II, III and IV) as shown in Figure 3.12.

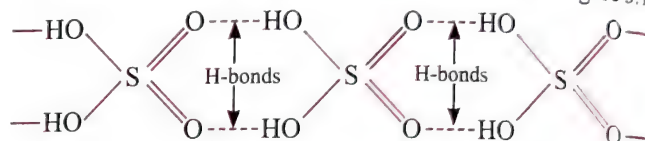
Fig. 3.12 Resonance of structure of SO_4^{2-} ion

3.14.3 PROPERTIES

Physical properties:

1. Pure concentrated sulphuric acid is a colourless syrupy liquid.
2. Concentrated sulphuric acid (98.3%) has a specific gravity of 1.84 at 298 K. It boils at 590 K and freezes into colourless crystals at 283 K.
3. It forms azeotrope, i.e., constant boiling mixture containing 98.3% H_2SO_4 and 1.7% water.
4. It is highly corrosive and produces burns on the skin (due to dehydration of skin).

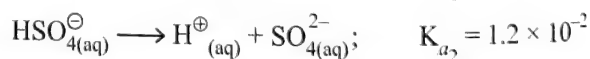
5. Sulphuric acid has a high boiling point (590 K) and a high viscosity because its molecules are associated due to intermolecular hydrogen bonding as shown in Figure 3.13.

Fig. 3.13 Intermolecular H-bonding in H_2SO_4

6. H_2SO_4 has a strong affinity for water various hydrates such as $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ are known. When sulphuric acid dissolves in water, a large amount of heat is produced which may spurt the acid out of the container. Hence, care must be taken while preparing dilute sulphuric acid from concentrated sulphuric acid (spurting of acid). Therefore conc. H_2SO_4 is always diluted by adding the acid slowly into water with constant stirring and not by adding water to acid.

Chemical properties:

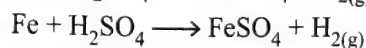
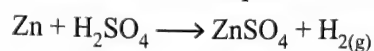
1. **Dissociation:** At 444°C (or 717 K), the vapours of H_2SO_4 dissociate into SO_3 and steam (H_2O).
2. **Acidic character:** In aqueous solution, H_2SO_4 ionises in two steps:



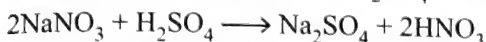
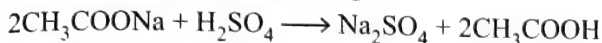
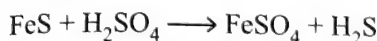
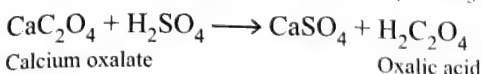
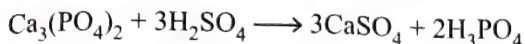
The larger value of K_{a1} ($K_{a1} > 10$) means that H_2SO_4 is largely dissociated into H^+ and HSO_4^- . Greater the value of dissociation constant (K_a), stronger is the acid.

Thus, H_2SO_4 acts as a strong dibasic acid and forms two series of salts – normal sulphates such as sodium sulphate (Na_2SO_4) and acid sulphates or hydrogen sulphates or bisulphates such as sodium bisulphate (NaHSO_4).

- a. It reacts with electropositive metals to evolved $\text{H}_{2(\text{g})}$



It displaces more volatile acids from their metal salts.



b. It forms two series of salts with bases.

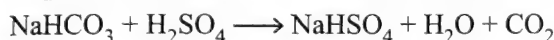
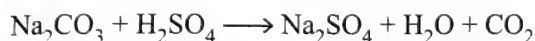


Sodium
bisulphate



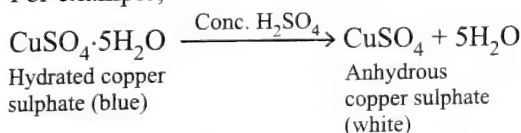
Sodium
sulphate

c. It decomposes carbonates and bicarbonates into carbon dioxide.

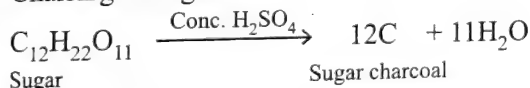


3. **Dehydrating agent:** As conc. H_2SO_4 has a strong affinity for water, it acts as a strong dehydrating agent. For example:

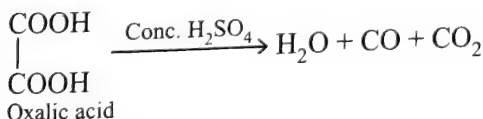
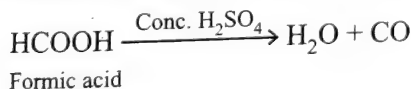
a. It removes water of crystallisation from hydrated salts. For example,



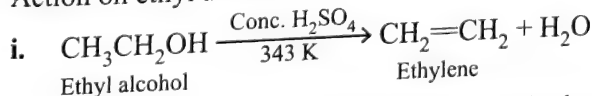
b. Charring of sugar



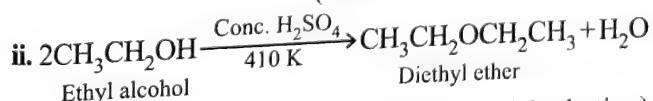
c. Dehydration of formic acid and oxalic acid



d. Action on ethyl alcohol



(Intramolecular dehydration)

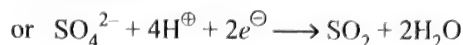
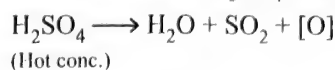


(Intermolecular dehydration)

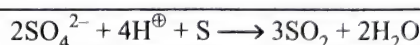
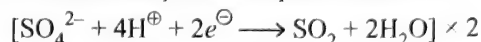
Drying of gases: Many gases such as O_2 , N_2 , Cl_2 , HCl , etc. which do not react with conc. H_2SO_4 can be dried by passing them through a bubbler containing conc. H_2SO_4 .

Cloth, wood, paper etc. are all charred in concentrated H_2SO_4 .

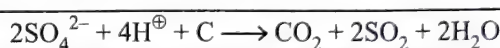
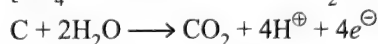
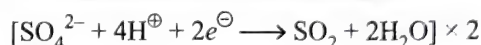
4. **Oxidising agent:** Hot concentrated sulphuric acid is a moderately strong oxidising agent since it on decomposition gives nascent oxygen, oxidising power of H_2SO_4 is intermediate between H_3PO_4 and HNO_3 .



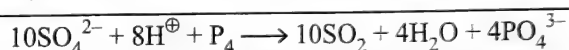
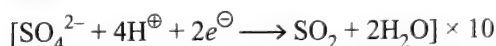
a. It oxidises sulphur to sulphur dioxide



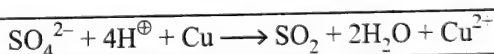
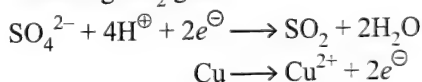
b. It oxidises carbon to carbon dioxide



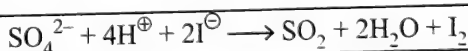
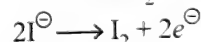
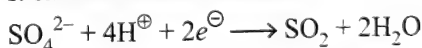
c. It oxidises phosphorous to phosphoric acid or phosphate ion



d. It oxidises metals such as Cu, Pb, Hg, Ag first to their oxides and then to their corresponding sulphates liberating SO_2 gas.

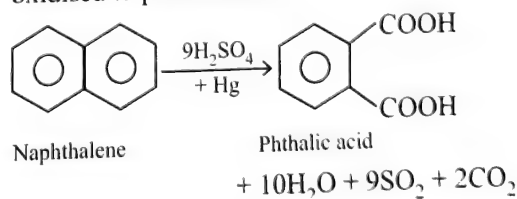


e. It oxidises iodide to iodine



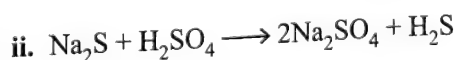
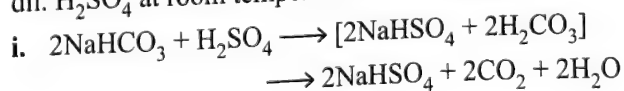
Similarly bromide is oxidised to bromine gas.

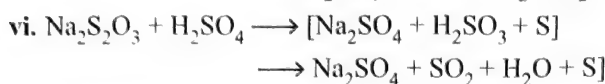
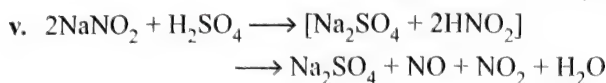
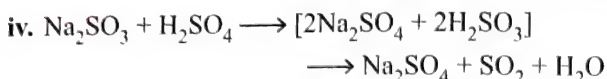
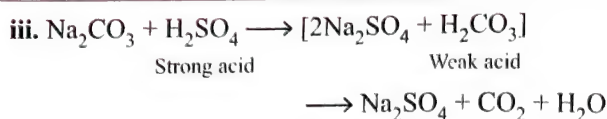
f. In the presence of Hg as a catalyst, naphthalene is oxidised to phthalic acid.



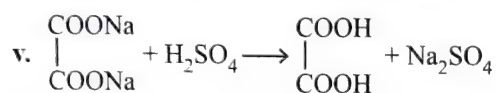
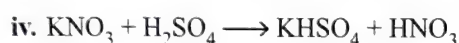
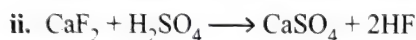
5. **Action on salts:** Due to its low volatility conc. H_2SO_4 can be used to manufacture more volatile acids from their corresponding salts.

a. **With dilute acid:** Bicarbonate, sulphides, carbonates, sulphites, thiosulphates and nitrites are decomposed by dil. H_2SO_4 at room temperature. For example,

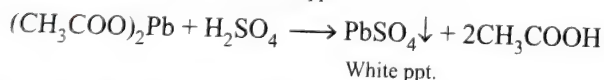
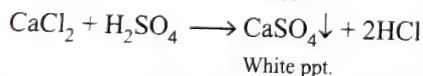
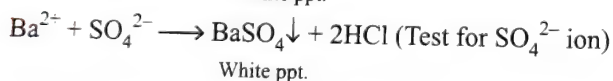
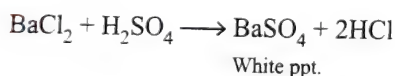




b. With hot concentrated acid: Chlorides, fluorides, acetates, nitrates and oxalates are decomposed by hot conc. H_2SO_4 liberating their corresponding acids. For example,

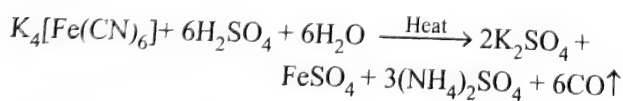


6. Precipitation reactions: When an aqueous solution of barium, strontium, calcium and lead salts are treated with dil. H_2SO_4 , white precipitate of their corresponding metal sulphates are formed, which are insoluble in conc. H_2SO_4 and conc. HNO_3 .

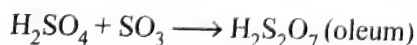


7. Miscellaneous reactions:

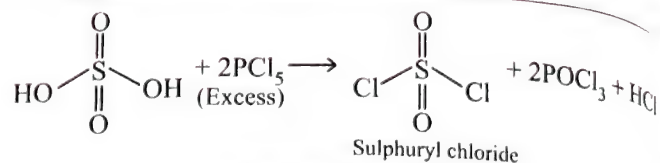
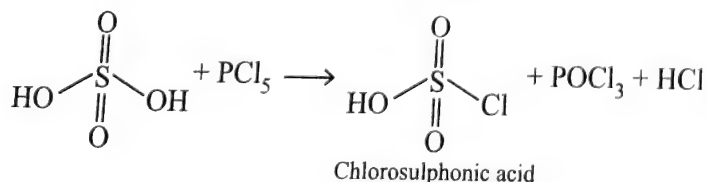
a. Reaction with potassium ferrocyanide: Carbon monoxide (CO) is formed on heating $\text{K}_4[\text{Fe}(\text{CN})_6]$ with H_2SO_4 .



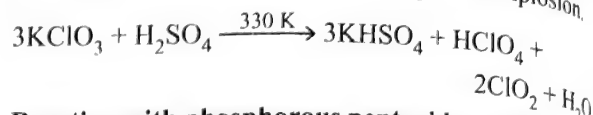
b. Reaction with sulphur trioxide: SO_3 dissolves in conc. H_2SO_4 forming oleum or fuming H_2SO_4 .



c. Reaction with PCl_5 : Depending upon the amount of PCl_5 used one or both the hydroxyl groups of H_2SO_4 can be replaced by chlorine atoms.



d. Reaction with KClO_3 : On heating with conc. H_2SO_4 , KClO_3 gives chlorine dioxide (ClO_2) with explosion,



e. Reaction with phosphorous pentoxide: H_2SO_4 reacts with phosphorous pentoxide to lose water and forms SO_3 .



3.14.4 USES

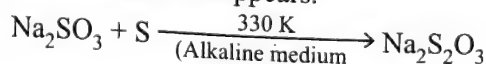
- 1. In chemical industry:** Sulphuric acid is employed in the manufacture of various chemicals such as hydrochloric acid, nitric acid, phosphoric acid, sulphates and bisulphates, diethyl ether, etc.
- 2. In dyes, drugs, paints, pigments and detergents:** It is used directly or indirectly in the manufacture of number of chemicals such as dyes, drugs, paints, pigments and detergents.
- 3. In fertiliser industry:** Sulphuric acid is used to manufacture fertilisers like ammonium sulphate and super phosphate of lime.
- 4. In the manufacture of explosives:** A mixture of sulphuric acid and nitric acid called nitrating mixture is used for nitration of organic compounds. This nitration process is used for the manufacture of a large number of explosives like dynamite (a mixture of glyceryl trinitrate and glyceryl dinitrate absorbed over Kieselguhr – a porous earth), gun cotton (nitrocellulose) T.N.T. (2,4,6-trinitrotoluene), picric acid (2,4,6-trinitrophenol), etc.
- 5. In petroleum refining:** Crude petroleum is treated with sulphuric acid to remove unwanted sulphur and other heavy compounds.
- 6. In metallurgy:** A number of metals like copper and silver are extracted from their ores using sulphuric acid.
- 7. In pickling.** Sulphuric acid is used for cleaning (pickling) the surface of metals before enamelling, electroplating and galvanising.
- 8. In leather industry for tanning.**
- 9. As laboratory reagent:** It is widely used in laboratory as a drying and dehydrating agent.
- 10. In lead storage batteries as electrolyte.**

3.15 COMPOUNDS OF SULPHUR

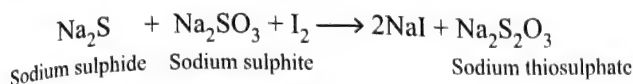
Sodium thiosulphate (Hypo) $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

Preparation:

- It is prepared by heating a solution of Na_2SO_3 with finally powdered sulphur in an alkaline medium until yellow colour due to sulphur disappears.



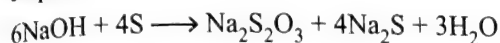
2. It can also be prepared by adding requisite amount of I_2 to a mixture of Na_2S and Na_2SO_3 (**Spring's reaction**).



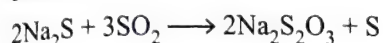
3. Pure $Na_2S_2O_3$ can be obtained by treating sodium bisulphite with sodium bisulphide followed crystallisation.



4. It was formerly manufactured by boiling $NaOH_{(aq)}$ with sulphur.

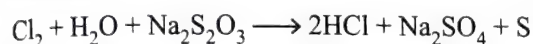


5. It can also be obtained by passing SO_2 through Na_2S solution.



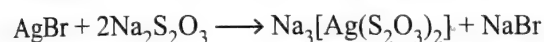
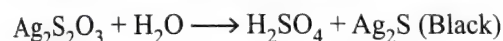
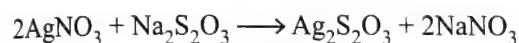
Properties: It is a white crystalline solid soluble in water.

1. **With Cl_2 or Br_2 :** Cl_2 (or Br_2) reacts with $Na_2S_2O_{3(aq)}$ as follows.



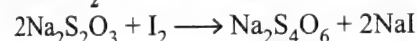
Hypo is thus used as an **antichlor** for removing excess Cl_2 in bleaching industry.

2. **With silver salts:**



This reaction has been used in photography to remove undecomposed silver halide on photographic film or paper.

3. **With I_2 :** This reaction is used in iodometric titrations.



Sodium tetrathionate

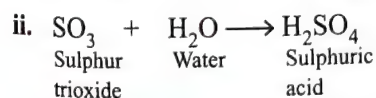
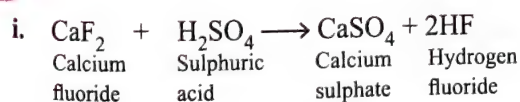
$Na_2S_2O_3$ so produced is colourless, hypo can be used to remove iodine stains from skin and clothes.

ILLUSTRATION 3.5

What happens when

- Concentrated H_2SO_4 is added to calcium fluoride.
- SO_3 is passed through water?

Sol.



SO_3 dissolves in water to form H_2SO_4 .

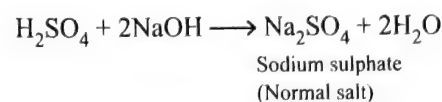
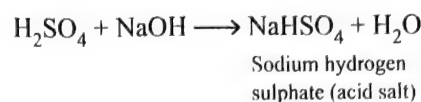
ILLUSTRATION 3.6

Give at least one example to explain the following properties

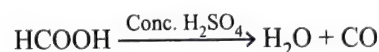
- Sulphuric acid is a dibasic acid.
- Sulphuric acid is a dehydrating agent.
- Sulphuric acid is an oxidising agent.

Sol.

- a. H_2SO_4 forms two series of salts, i.e., both the hydrogen atoms are replaceable.



- b. H_2SO_4 has great affinity for water molecules and hence, acts as a dehydrating agent.



- c. H_2SO_4 oxidises metals, non-metals and other compounds.

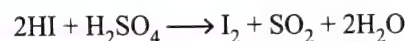
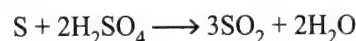
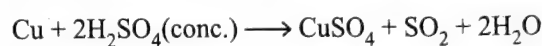


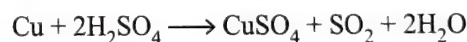
ILLUSTRATION 3.7

How will you obtain the following from sulphuric acid?

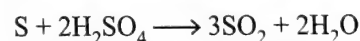
- SO_2
- SO_3
- SO_2Cl_2

Sol.

- a. SO_2 is obtained by heating copper with conc. H_2SO_4 .



It can also be obtained by boiling sulphur with conc. H_2SO_4 .



- b. H_2SO_4 when titrated with P_2O_5 loses water and forms SO_3 .



- c. SO_2Cl_2 is formed when conc. H_2SO_4 is treated with excess of PCl_5 .

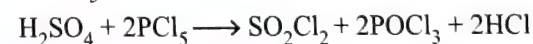


ILLUSTRATION 3.8

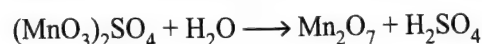
Give reason for the following:

- Conc. H_2SO_4 cannot be used for drying H_2 .
- $KMnO_4$ should not be dissolved in conc. H_2SO_4 .

Sol.

- a. Hydrogen sometimes ignites with the large amount of heat released when water is absorbed by conc. H_2SO_4 .

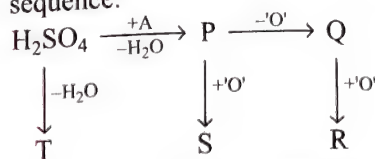
- b. Mn_2O_7 is formed when $KMnO_4$ is dissolved in conc. H_2SO_4 . Mn_2O_7 formed is highly unstable and explosive in nature.



CONCEPT APPLICATION EXERCISE 3.1

- An aqueous solution of a gas (X) gives the following reactions:
 - It decolourises an acidified $K_2Cr_2O_7$ solution.
 - On boiling with H_2O_2 , cooling it and then adding an aqueous solution of $BaCl_2$, a precipitate insoluble in conc. HCl is obtained.
 - On passing H_2S in the solution, white turbidity is obtained.
 Identify (X) and give equations for steps (a), (b) and (c).
- An inorganic halide (A) reacts with water to form two acids (B) and (C). (A) also reacts with $NaOH$ to form two salts (D) and (E) which remain in solution. The solution gives white precipitate with both $AgNO_3$ and $BaCl_2$ solutions respectively. (A) is a useful organic reagent. Identify (A) to (E).
- Name the following compounds:
 - Oxides of sulphur:**
 - S_2O
 - S_2O_3
 - SO_4
 - S_2O_7
 - Oxyacids of sulphur:**
 - H_2SO_2
 - H_2SO_3
 - $H_2S_2O_4$
 - $H_2S_2O_2$
 - $H_2S_2O_5$
 - Sulphuric acids:** (i) $H_2S_2O_3$ (ii) $H_2S_2O_7$
 - Thionic acids:** (i) $H_2S_2O_6$ (ii) $H_2(S)_nO_6$
 - Peroxo acids:** (i) H_2SO_5 (ii) $H_2S_2O_8$
- Explain the following:
 - An acidified $K_2Cr_2O_7$ paper turns green when exposed to SO_2 .
 - H_2S acts only as reducing agent while SO_2 can act both as a reducing agent and an oxidising agent.
 - SO_2 acts as a bleaching agent.
 - Sugar turns black on addition of conc. H_2SO_4 .
 - Ozone destroys mercury meniscus.
 - SF_6 is known, but SH_6 is not known.
- What happens when:
 - Ozone is passed through acidified stannous chloride solution.
 - Potassium iodide is heated with conc. H_2SO_4 .
 - Sulphur is boiled with caustic soda solution.
 - Ozone reacts with potassium ferrocyanide solution.
 - Ozone is treated with ethylene.
 - Sulphur dioxide is bubbled through aqueous solution of copper sulphate in presence of potassium thiocyanate.
 - Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride.
 - Sulphuric acid is treated with PCl_5 .
- When sulphur is boiled with Na_2SO_3 , a compound (X) is produced. (X) with excess of $AgNO_3$ solution gives a compound (Y) which is soluble in water and produces a black coloured sulphide (Z). Identify compounds (X), (Y) and (Z).

- Identify the products (P + OT) in the following reaction sequence:



- The following compounds on complete hydrolysis at room temperature gives the products.
 - SF_4
 - $H_2S_2O_8$
 Identify the products which acts as:
 - Dibasic acid
 - Monodentate ligand
 - Flexidentate ligand
 - Both oxidising and reducing agents.
 - Non-redox hydrolysis.
- Complete the following equations:
 - $(NH_4)_2S_2O_8 + H_2O + MnSO_4 \longrightarrow \dots + \dots + \dots$
 - $S + H_2SO_4(\text{conc.}) \xrightarrow{\text{Heat}} \dots + H_2O$
 - $I_2 + SO_2 + H_2O \longrightarrow SO_4^{2-} + \dots + H^+$
 - $I_2 + O_3 + H_2O \longrightarrow HIO_3 + \dots$
 - $Cr_2O_7^{2-} + H^+ + SO_2 \longrightarrow SO_4^{2-} + H_2O + \dots$
 - $H_2S + HNO_3 \longrightarrow \dots + H_2O + S$
- An organic acid (A) reacts with concentrated H_2SO_4 to give a neutral oxide (B), acidic oxide (C) and a diatomic oxide (D). When (D) reacts with chlorine gas, a poisonous gas (E) is evolved. This gas with ammonia gives an organic compound (F). The compounds (A) and (F) are
- Compounds A and B are treated with dilute HCl separately. The gases liberated are Y and Z respectively. Y turns acidified $K_2Cr_2O_7$ paper green while Z turns lead acetate paper black. The compounds A and B are respectively.
- The following oxides are given, if $x = \text{number of neutral oxides}$.
 $NO, N_2O, N_2O_5, P_2O_5, CO, H_2O, SrO, SO_3, Cl_2O_7$
 - The general formula for polythionic acid series is $H_2S_yO_6$. If y is the value for hexathionic acid.
 - If z is number of SOS bond in S_3O_9 , then calculate the value of expression $x + y - z$.

Solved Examples

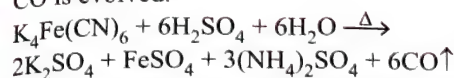
EXAMPLE 3.1

State with balanced equation what happens when?

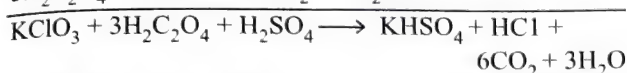
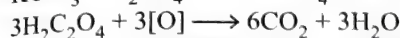
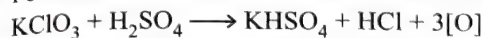
- Potassium ferrocyanide is heated with conc. H_2SO_4 .
- A mixture of potassium chlorate, oxalic acid and sulphuric acid is heated.
- Sodium chlorate reacts with sulphur dioxide.
- Chlorine gas is passed into water saturated with hydrogen sulphide.
- Hydrogen sulphide is passed through sodium bisulphite solution.

Sol.

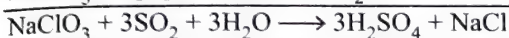
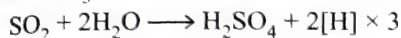
- a. CO is evolved.



- b. Potassium chlorate is reduced while oxalic acid is oxidised.

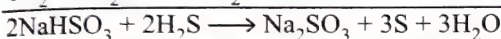


- c. NaClO_3 is reduced to NaCl .



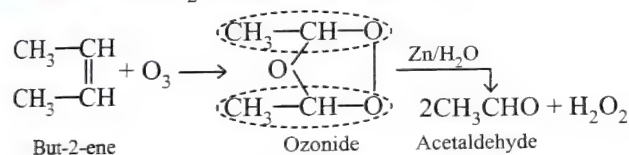
- d. $\text{Cl}_2 + \text{H}_2\text{S} \longrightarrow 2\text{HCl} + \text{S}$

- e. $2\text{NaHSO}_3 \longrightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{SO}_2$

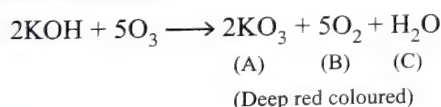
**EXAMPLE 3.2**

When gas A is passed through dry KOH at low temperature, a deep red coloured compound, B and a gas C are obtained. The gas A, on reaction with but-2-ene, followed by treatment with $\text{Zn}/\text{H}_2\text{O}$ yields acetaldehyde. Identify A, B and C.

Sol. The reaction of gas A with but-2-ene followed by treatment with $\text{Zn}/\text{H}_2\text{O}$ suggests that A is O_3 .



Reaction with KOH



Hence A is O_3 , B is KO_3 and C is O_2 .

EXAMPLE 3.3

- a. Sulphur melts to form a clear mobile liquid at 119°C but on further heating to 180°C , it becomes viscous. Why?
- b. SOCl_2 can act as a weak Lewis acid as well as a weak Lewis base. Explain.

Sol.

- a. Up to 119°C , sulphur exists as S_8 molecules which can roll over one another to form a mobile liquid. However, when this liquid is further heated to 180°C , the cleavage of ring structure occurs and zig-zag open chains are formed which get interwound and tangled together and hence sulphur becomes more viscous.

- b. Like nitrogen in ammonia, sulphur has two lone pair of electrons which it can donate, hence it acts as a weak base.

SOCl_2 has also empty d -orbitals which can accommodate electron pairs from bases and hence acts as a weak acid.

EXAMPLE 3.4

Concentrated H_2SO_4 is added to the test tubes containing (a) to (e).

Test tube	Compounds
a.	Cane sugar
b.	Sodium bromide
c.	Copper turnings
d.	Sulphur powder
e.	Potassium chloride

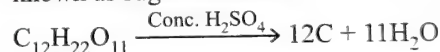
Identify in which of the above test tubes, the following change will be observed on heating. Also give the chemical equations involved.

- Formation of black substance.
- Evolution of brown gas.
- Evolution of colourless gas.
- Formation of brown substance, which on dilution becomes blue.
- Disappearance of yellow powder along with the evolution of a colourless gas.

Sol.

- i. Conc. H_2SO_4 + Cane sugar $\xrightarrow{\Delta}$ Black substance

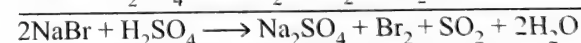
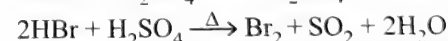
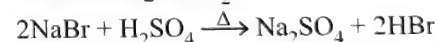
Conc. H_2SO_4 acts as a dehydrating agent, hence it removes water from cane sugar on heating and forms a black substance known as sugar charcoal.



Thus, formation of black substance occurs in test tube (a).

- ii. Conc. H_2SO_4 + sodium bromide $\xrightarrow{\Delta}$ Brown gas

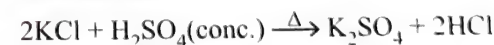
On heating NaBr along with conc. H_2SO_4 , brown gas Br_2 is evolved. Initially HBr is produced, as HBr is a moderate reducing agent, it reduces H_2SO_4 to SO_2 and itself is oxidised to bromine gas, Br_2 .



Thus, evolution of brown gas occurs in test tube (b).

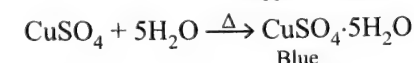
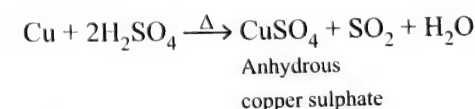
- iii. Potassium chloride + conc. H_2SO_4 $\xrightarrow{\Delta}$ colourless gas

KCl on heating with conc. H_2SO_4 , liberates HCl gas which is colourless.



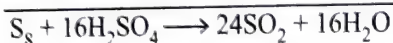
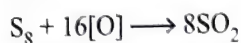
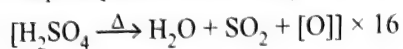
Since HCl is not a reducing agent, it does not reduce H_2SO_4 to SO_2 . Thus evolution of colourless gas occurs in test tube (e).

- iv. Cu turnings + conc. $\xrightarrow{\Delta}$ Brown substance $\xrightarrow{\text{H}_2\text{O}}$ Blue soln.



On heating, Cu turnings with conc. H_2SO_4 , a brownish substance, i.e. a mixture of Cu turnings and white anhydrous copper sulphate is formed along with evolution of pungent smelling SO_2 gas. On dilution, the solution turns blue due to the formation of hydrated copper sulphate which is soluble in water. Hence, formation of brown substance, which on dilution becomes blue occurs in test tube (c).

v. Sulphur powder + conc. $\text{H}_2\text{SO}_4 \xrightarrow{\Delta}$



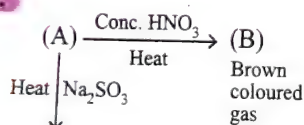
Yellow powder	Colourless pungent smelling gas
------------------	---------------------------------------

v. On heating sulphur powder, which is yellowish in colour with conc. H_2SO_4 , pungent smelling colourless, SO_2 gas is produced, thus yellow powder disappears and the above reaction will occur in test tube (d).

EXAMPLE 3.5

A pale yellow substance (A) when heated with conc. HNO_3 evolves a brown coloured gas (B). The substance (A) also dissolves in sodium sulphite solution on heating. A clear solution (C) is formed which on acidification gives a turbid solution and a pungent smelling gas (D) which is formed by the substance (A) in air. The solution (C) decolourises iodine solution. Identify (A) to (D).

Sol.



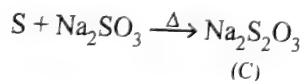
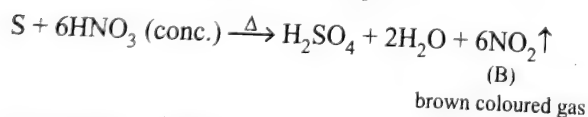
(A) dissolve

to form (C) $\xrightarrow{\text{Acidification}}$ Turbid + Pungent smelling solution gas (D)

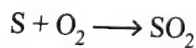
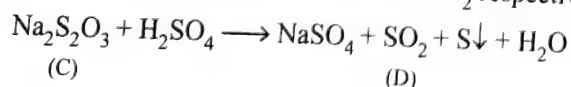
(A) $\xrightarrow{\text{air}}$ (D)

(C) soln. + I_2 soln. \longrightarrow Decolourisation of I_2 soln.

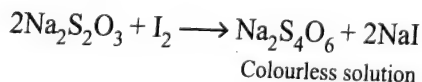
Pale yellow substance (A) is sulphur.



$\text{Na}_2\text{S}_2\text{O}_3$, on acidification, gives a turbid solution and a pungent smelling gas due to formation of S and SO_2 respectively.



(A) (air) (D)



Since I_2 is reduced to I^- , a colourless solution is formed.

EXAMPLE 3.6

In the following oxyanions:

i. SO_4^{2-} ii. $\text{S}_2\text{O}_5^{2-}$ iii. $\text{S}_2\text{O}_7^{2-}$ iv. $\text{S}_3\text{O}_6^{2-}$

If X = Number of oxyanions having two equivalent S-O bonds per central atom.

Y = Number of oxyanions having three equivalent S-O bonds per central atom.

Z = Number of oxyanions having four equivalent S-O bonds per central atom.

Find the value of X + Y + Z.

Sol.

Oxyanions Sulphate ion (SO_4^{2-})	No. of equivalent bonds
i.	X = 2
ii. Pyrosulphite ion ($\text{S}_2\text{O}_5^{2-}$) 	X = 2 Y = 3
iii. Pyrosulphate ion ($\text{S}_2\text{O}_7^{2-}$) 	Y = 3
iv. Trithionate ion ($\text{S}_3\text{O}_6^{2-}$) 	Y = 3
$X + Y + Z = (2 + 2) + (3 + 3 + 3) + 0 = 12$	

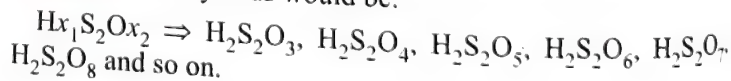
EXAMPLE 3.7

The oxyacid are represented as $\text{Hx}_1\text{S}_2\text{Ox}_2$, where x_1 and x_2 are natural numbers.

If there are three possible oxyacid of sulphur, A, B and C and ratio of $x_2 : x_1$ are 2, 3 and 4 respectively. Calculate the sum of oxidation state of 'S' atom in three oxyacids.

Sol. For any oxyacid of 'S' atom number of H-atom = 2.

Formula of oxyacids would be:



$$\text{For } \text{H}_2\text{S}_2\text{O}_4; \frac{x_2}{x_1} = \frac{4}{2} = 2$$

Oxidation state (O.S.) of 'S' = +3

$$\text{For } \text{H}_2\text{S}_2\text{O}_6; \frac{x_2}{x_1} = \frac{6}{2} = 3$$

O.S. of 'S' atom = +4

$$\text{For } \text{H}_2\text{S}_2\text{O}_8; \frac{x_2}{x_1} = \frac{8}{2} = 4$$

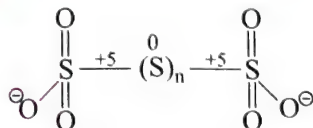
O.S. of 'S' atom = +6

$$\text{Sum of O.S.} = 3 + 4 + 6 = 13$$

EXAMPLE 3.8

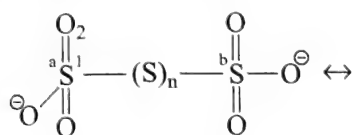
The general formula of polythionate ion is $S_{n+2}O_6^{2-}$. If average oxidation state of 'S' atom in any polythionate ion is equal to bond order of 'S-O' bond. Then calculate the value of 'n' for the corresponding polythionate ion.

Sol. Structure of polythionate ion is:

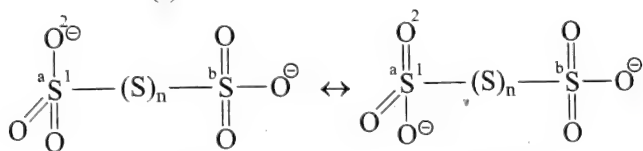


(No. of resonating structure = 3)

Resonating structures are:



(I)



(II)

(III)

(Similar resonating structures are obtained from 'S' atom 'b' therefore total resonating structures = 3.

(Two bonded atoms selected as 1 and 2).

$$\text{Bond order} = \frac{\text{Total no. of bonds between two atoms in all the structures}}{\text{Total no. of resonating structures}}$$

(Any two bonded atoms may be selected and a double bond will mean two bonds and a triple bond means three bonds).

$$\text{Bond order} = \frac{\text{Double bond in (I) + Double bond in (III) + single bond in II}}{\text{Total resonating structures}}$$

$$= \frac{2(\text{in I}) + 2(\text{in III}) + 1(\text{in II})}{3}$$

$$= \frac{5}{3} = 1.66.$$

$$\therefore \text{Bond order of (S-O) bond} = 1.66 \text{ or } \left(\frac{5}{3}\right)$$

$$\begin{aligned} \text{Average O.S of 'S' atom} &= \frac{\text{Total O.S.}}{\text{No. of S-atom}} \\ &= \frac{+5 + 5}{n+2} = \frac{10}{n+2} \end{aligned}$$

$$\text{Thus } \frac{10}{n+2} = \frac{5}{3} \text{ (Bond order)}$$

$$n+2 = 6$$

$$n = 4.$$

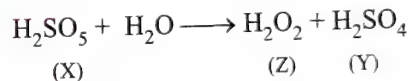
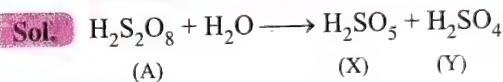
EXAMPLE 3.9

Peroxydisulphuric acid (A) on partial hydrolysis gives two acid (X) and (Y).

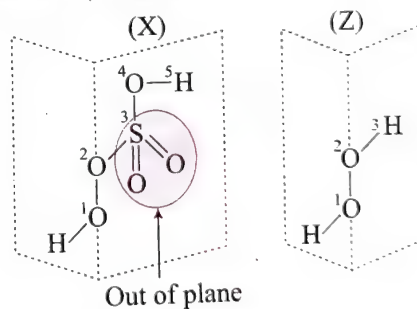
Acid (X) on hydrolysis a compound (Z) and acid (Y).

If Q and R represent maximum number of atoms that can lie in a plane of acid (X) and compound (Z).

Then find the value of $\frac{Q+R}{2}$.



Structures of (X) and (Z) are:



No. of atoms in a plane = 5 = Q

No. of atoms in a plane = 3 = R

$$\therefore \frac{Q+R}{2} = \frac{5+3}{2} = 4$$

Exercises

Single Correct Answer Type

Physical and Chemical Properties

- Which one of the following has the highest bond energy?
 - O–O
 - S–S
 - Se–Se
 - Te–Te
- Which one has the highest and lowest boiling point?
 - H₂O, H₂S
 - H₂O, H₂Se
 - H₂S, H₂O
 - H₂S, H₂Se
- Which one of the following is strongest acid?
 - H₂S
 - H₂Se
 - H₂O
 - H₂Te
- Which one has the lowest boiling point?
 - H₂O
 - H₂S
 - H₂Se
 - KNO₃
- Anomalous behaviour of oxygen is due to
 - It is highly electronegative
 - Small atomic size
 - Non-availability of *d*-orbitals
 - All
- Which shows maximum catenation property?
 - Se
 - Te
 - Po
 - S
- Which one of the following is **wrong**?
 - Oxygen and sulphur belong to the same group of periodic table
 - Oxygen is a gas while sulphur is solid
 - Both oxygen and sulphur show +2, +4 and +6 oxidation states
 - H₂S has no hydrogen bonding
- Non-metals combine with oxygen to form usually
 - Basic oxides
 - Neutral oxides
 - Acidic oxides
 - Amphoteric oxides
- Sulphur does not exist as S₂ molecule because
 - It is less electronegative
 - It has ability to exhibit catenation
 - It is not able to constitute *pπ–pπ* bond
 - It has the tendency to show variable oxidation states
- The element evolving two different gases on reaction with conc. H₂SO₄
 - P
 - C
 - Hg
 - S
- Sulphur reacts with chlorine in 1:2 ratio and forms (X). (X) on hydrolysis gives a sulphur compound (Y). What is the hybridised state of central atom in the anion of (Y)?
 - sp*
 - sp*³
 - sp*²
 - sp*³*d*
- Gas that cannot be collected over water is:
 - N₂
 - O₂
 - SO₂
 - PH₃
- One gas bleaches the colour of flowers by reduction, while the other by oxidation, the two gases respectively are:
 - CO and Cl₂
 - NH₃ and SO₃
 - H₂S and Br₂
 - SO₂ and Cl₂
- Which pair of elements can form multiple bond with itself and oxygen?
 - F, N
 - N, Cl
 - N, P
 - N, C
- Which of the following is the correct order of melting points of group 16 elements?
 - O < S < Se < Te < Po
 - O < S < Se < Te ≈ Po
 - O < S < Se < Te > Po
 - O < S < Se > Te < Po
- Which of the following elements(s) are known as photosensitive elements?
 - Te
 - Se
 - Both (1) and (2)
 - None of these
- The correct order of acidic nature of trioxide is
 - SO₃ > SeO₃ > TeO₃
 - SO₃ > TeO₃ > SeO₃
 - TeO₃ > SO₃ > SeO₃
 - SO₃ < SeO₃ < TeO₃
- Which of following represents the correct order of melting point of hydrides of group-16?
 - H₂O > H₂S > H₂Se > H₂Te
 - H₂O > H₂S > H₂Te > H₂Se
 - H₂O > H₂Te > H₂Se > H₂S
 - H₂O > H₂Se > H₂Te > H₂S
- Stability of tetrabromides follows the order
 - SeBr₄ < TeBr₄ < PoBr₄
 - SeBr₄ < PoBr₄ < TeBr₄
 - PoBr₄ < TeBr₄ < SeBr₄
 - None of these
- Correct order of hydrolysis of hexa-fluorides is
 - TeF₆ > SeF₆ > SF₆
 - SF₆ > SeF₆ > TeF₆
 - SF₆ > TeF₆ > SeF₆
 - None of these
- Which of the following is correctly represents increasing order of reducing nature of hybrids?
 - H₂S < H₂Se < H₂Te
 - H₂S < H₂Te < H₂S
 - H₂Se < H₂S < H₂Te
 - H₂Te < H₂Se < H₂S

Compounds of Oxygen

- Which of the following compounds does not evolve oxygen when heated alone?
 - KClO₃
 - KMnO₄
 - NH₄NO₂
 - KNO₃
- When oxygen is passed through a solution of Na₂SO₃, we get
 - Na₂S
 - Na₂SO₄
 - NaHSO₄
 - NaH
- The product A in the following reaction:

$$2\text{KMnO}_4 \longrightarrow \text{A} + \text{KMnO}_2 + \text{O}_2$$
 is

- (1) $K_2Mn_2O_7$ (2) K_2MnO_4
 (3) K_2O (4) K_2O_2
25. The gases respectively absorbed by alkaline pyrogallol and oil of cinnamon is
 (1) O_3 , CH_4 (2) SO_2 , CH_4
 (3) O_2 , O_3 (4) N_2O , O_3
26. Ozone reacts with $K_4Fe(CN)_6$ to form
 (1) Fe_2O_3 (2) $Fe(OH)_3$
 (3) $Fe(OH)_2$ (4) $K_3Fe(CN)_6$
27. Which one of the following is **not true** peroxide?
 (1) PbO_2 (2) BaO_2
 (3) Na_2O_2 (4) H_2O_2
28. Which one of the following is an amphoteric oxide?
 (1) MnO_2 (2) ZnO
 (3) CaO (4) CO_2
29. On heating ozone, its volume
 (1) Increases to 1.5 times (2) Decreases to half
 (3) Remain unchanged (4) Becomes double
30. In the reaction,
 $2KI + H_2O + O_3 \longrightarrow 2KOH + O_2 + A$
 the compound A is
 (1) KIO_3 (2) I_2O_5
 (3) HIO_3 (4) I_2
31. Select the **incorrect** statement about the following:
 (1) O_3 is used as germicide for purification of air
 (2) In O_3 , O—O bond length is identical with that of molecular oxygen
 (3) O_3 molecule is angular in shape
 (4) O_3 is an oxidising agent
32. The correct order of O—O bond length in O_2 , H_2O_2 and O_3
 (1) $O_3 > H_2O_2 > O_2$ (2) $O_2 > H_2O_2 > O_3$
 (3) $O_2 > O_3 > H_2O_2$ (4) $H_2O_2 > O_3 > O_2$
33. Which of the following is not correct?
 (1) $3O_2 \xrightleftharpoons[\text{Discharge}]{\text{Silent electric}} 2O_3$; $\Delta H = -284.5 \text{ kJ}$
 (2) Ozone undergoes addition reaction with unsaturated carbon compounds.
 (3) Sodium thiosulphate reacts with I_2 to form sodium tetrathionate and sodium iodide.
 (4) Ozone oxidises lead sulphide to lead sulphate
34. Tailing of mercury test can be used for which of the following gas?
 (1) Dioxygen (2) Dihydrogen
 (3) Dinitrogen (4) Ozone
35. Which gas is used to improve the atmosphere of the crowded places?
 (1) H_2 (2) O_2
 (3) O_3 (4) N_2O
36. By which of the following methods, H_2O_2 can't synthesized?
 (1) Aerial oxidation of 2-ethyl anthraquinol
 (2) Addition of ice cold H_2SO_4 on PbO_2
 (3) Lewis addition of ice cold H_2SO_4 on BaO_2
 (4) Electrolysis of $(NH_4)_2SO_4$ at a high current density
37. Estimation of ozone can be made quantitatively by
 (1) Decomposition into O_2 and absorption of O_2 into pyrogallol
 (2) Volumetric method using KI and titration of the liberated iodine using hypo solution
 (3) Oxidative ozonolysis method
 (4) All methods give above
38. A green coloured solution of same salt changes its colour to light pink on passing ozone through it. Which of the following species represent pink and green colour respectively?
 (1) MnO_4^{2-} and MnO_4^- (2) Mn^{2+} and MnO_2
 (3) MnO_4^- and MnO_4^{2-} (4) Cu^+ and Cu^{2+}
39. Which of the following reaction is carried out to obtain pure oxygen?
 (1) By the action of water on oxone
 (2) By heating alkali nitrates
 (3) By heating $KMnO_4$ or $K_2Cr_2O_7$ with conc. H_2SO_4
 (4) By adding H_2O_2 to acidified $KMnO_4$ solution

Compounds of Sulphur

40. Which has greater reactivity
 (1) $TeCl_6$ (2) SF_6
 (3) TeF_6 (4) SeF_6
41. SO_3 exists in
 (1) 3 forms (2) 2 forms
 (3) 4 forms (4) Only one
42. H_2SO_3 and H_2SO_4 involve hybridisation of the type
 (1) Both sp^3 (2) Both sp^3d
 (3) sp^3 , sp^3d (4) Both dsp^2
43. Sulphuric acid has great affinity for water because it
 (1) Decomposes water (2) Forms hydrate with water
 (3) Hydrolyse the acid (4) Decomposes the acid
44. High density and low volatility of H_2SO_4 is due to
 (1) Strong bonds (2) van der Waals force
 (3) Hydrogen bonding (4) None
45. Conc. H_2SO_4 is not a
 (1) Dehydration agent (2) Hygroscopic
 (3) Oxidising agent (4) Efflorescent
46. In the following reaction, H_2SO_4 acts as
 $HCOOH \xrightarrow{H_2SO_4} CO + H_2O$
 (1) Dehydrating agent (2) Oxidising agent
 (3) Reducing agent (4) All
47. Oxalic acid when heated with conc. H_2SO_4 it gives out
 (1) H_2O and CO_2 (2) Oxalic sulphate
 (3) CO_2 and H_2S (4) CO and CO_2
48. In the following reaction, H_2SO_4 acts as
 $2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + 2H_2O + SO_2$

- (1) Reducing agent (2) Oxidising agent
(3) Catalytic agent (4) Dehydration agent
49. A boy accidentally splashes a few drops of conc. H_2SO_4 on his cotton shirt and splashed part blackens and holes appears. This is because the sulphuric acid
- (1) Heats up the cotton so that it burns
(2) Dehydrates the cotton
(3) Causes the cotton to react with oxygen in air
(4) Removes the elements of water from cotton
50. Hypo is used in photography because of its
- (1) Complexing ability (2) Solubility in water
(3) Reducing behaviour (4) Sensitivity to light
51. Caro's and Marshall's acid does not react with
- (1) S (2) KMnO_4
(3) KI (4) H_2O
52. Sulphur dioxide is obtained by the action of dilute H_2SO_4 on:
- (1) Copper turning (2) Sodium sulphate
(3) Sodium sulphite (4) Sodium sulphide
53. Moist iodine reacts with ozone to form
- (1) HI (2) I_2O_5
(3) HIO_3 (4) HIO_4
54. The ratio of the gases obtained on dehydration of HCOOH and $\text{H}_2\text{C}_2\text{O}_4$ by conc. H_2SO_4 is
- (1) 2 : 1 (2) 1 : 2
(3) 3 : 1 (4) 1 : 3
55. When SO_2 is passed through a solution of H_2S in water:
- (1) Sulphuric acid is formed (2) A clear solution is formed
(3) Sulphur is precipitated (4) No change is observed
56. SF_6 is unreactive towards water because
- (1) Sulphur has very small size
(2) Fluorine is most electronegative element
(3) Sulphur shows +6 oxidation state
(4) Due to steric hindrance, molecule cannot attack S-atom
57. From the following information
- $\text{X} + \text{H}_2\text{SO}_4 \longrightarrow \text{Y}$ (a colourless and irritating gas)
 $\text{Y} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \longrightarrow$ green coloured solution
 Identify the pair X and Y.
- (1) Cl^- , HCl (2) SO_3^{2-} , SO_2
(3) S^{2-} , H_2S (4) CO_3^{2-} , CO_2
58. Which one of the following statements is **wrong**?
- (1) SO_2 dissolves in water and forms sulphurous acid
(2) SO_2 acts as a bleaching agent
(3) SO_2 has pungent odour
(4) SO_2 acts only as oxidising agent
59. Which of the following acts as pickling agent?
- (1) HNO_3 (2) H_2SO_4
(3) HCl (4) HNO_2
60. Excess of PCl_5 reacts with conc. H_2SO_4 gives
- (1) Sulphuryl chloride (2) Sulphurous acid
(3) Chlorosulphonic acid (4) Thionyl chloride
61. The number of sigma and pi bonds in peroxydisulphuric acid are, respectively
- (1) 9 and 4 (2) 11 and 4
(3) 4 and 8 (4) 4 and 9
62. Which of the following solutions does not change its colour on passing ozone through it?
- (1) Starch iodide solution
(2) Alcoholic solution of benzidine
(3) Acidic solution of $\text{K}_2\text{Cr}_2\text{O}_7$
(4) Acidified solution of FeSO_4
63. Hydrolysis of one mole of peroxydisulphuric acid produces
- (1) Two moles of sulphuric acid
(2) Two moles of peroxymonosulphuric acid
(3) One mole of sulphuric acid and one mole of peroxymonosulphuric acid
(4) One mole of sulphuric acid, one mole of peroxymonosulphuric acid and one mole of hydrogen peroxide
64. When an inorganic compound reacts with SO_2 in aqueous medium produces (A). (A) on reaction with Na_2CO_3 gives the compound (B) which with sulphur gives a substance (C) used in photography. The compound (C) is
- (1) $\text{Na}_2\text{S}_2\text{O}_3$ (2) Na_2SO_4
(3) Na_2S (4) $\text{Na}_2\text{S}_2\text{O}_7$
65. Identify the correct sequence of increasing number of π -bonds in structures of the following molecules.
- (I) $\text{H}_2\text{S}_2\text{O}_6$ (II) H_2SO_3 (III) $\text{H}_2\text{S}_2\text{O}_5$
- (1) I, II, III (2) II, III, I
(3) II, I, III (4) I, III, II
66. Which of the following reactions depict the oxidizing behaviour of H_2SO_4 ?
- (1) $2\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
(2) $2\text{PCl}_5 + \text{H}_2\text{SO}_4 \longrightarrow 2\text{POCl}_3 + 2\text{HCl} + \text{SO}_2\text{Cl}_2$
(3) $2\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
(4) $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl}$
67. The oxidation state of sulphur in the anions SO_3^{2-} and $\text{S}_2\text{O}_8^{2-}$ follows the order:
- (1) $\text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-} < \text{SO}_3^{2-}$ (2) $\text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-} < \text{S}_2\text{O}_8^{2-}$
(3) $\text{SO}_3^{2-} < \text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-}$ (4) $\text{S}_2\text{O}_6^{2-} < \text{SO}_4^{2-} < \text{SO}_3^{2-}$
68. In presence of moisture, SO_2 acts as a good reducing agent. Which of the following statement is correct.
- (1) It turns orange coloured potassium dichromate solution green.
(2) It decolourises pink violet colour of acidified KMnO_4 solution, as SO_2 reduces MnO_4^- to Mn^{2+}
(3) Both (1) and (2)
(4) None of these
69. Which of the following halides cannot be hydrolyzed at room temperature?
- (I) TeF_6 (II) SF_6
(III) NCl_3 (IV) NF_3

Choose the correct code:

- (1) III and IV (2) I, II and III
(3) I, II and IV (4) II and IV

70. Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false.

- (I) Number of S—S bonds in $H_2S_nO_6$ are $(n + 1)$
(II) When F_2 reacts with water gives HF , O_2 and O_3
(III) $LiNO_3$ and $BaCl_2$ compounds are used in fire works
(IV) Be and Mg hydrides are ionic and polymeric

- (1) FTTF (2) TTFF
(3) FTTT (4) TFTT

71. Which of the following parent oxyacid does not have its hypo acid?

- (1) HNO_2 (2) H_2SO_3
(3) $HClO_3$ (4) H_3PO_3

72. Consider the following reactions:

- (i) $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$
(ii) $SF_4 + 3H_2O \longrightarrow H_2SO_3 + 4HF$
(iii) $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$
(iv) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

Then according to given information the incorrect statement is:

- (1) During the (iv) reaction the hybridization of 18th group element does not change
(2) During the (iii) reaction the hybridization of 13th group element does not change
(3) During the (ii) reaction the hybridization of 16th group element has been changed
(4) During the (i) reaction the hybridization of 15th group element does not change

73. The correct order of S—S bond length in following oxyanions is:

- (I) $S_2O_4^{2-}$ (II) $S_2O_5^{2-}$ (III) $S_2O_6^{2-}$
(1) $I > II > III$ (2) $III > II > I$
(3) $III > I > II$ (4) $I > III > II$

74. In which of the following reaction product does not contain 'Peroxy' linkage?

- (1) $H_4P_2O_8 \xrightarrow{+H_2O}$ (2) $2Na \xrightarrow[\Delta]{\text{excess } O_2}$
(3) $2OF \xrightarrow{\text{Dimerization}}$ (4) None of these

75. Consider the following statements in respect of oxides of sulphur

- (I) In gas phase SO_2 molecule is V-shape.
(II) In gas phase SO_3 molecule is planar.
(III) γ - SO_3 is cyclic trimer.
(1) I & II only (2) II and III only
(3) I & III only (4) I, II and III

76. In thiosulphuric acid:

- (1) there is only one replaceable hydrogen atom
(2) one S atom is in +2 and other sulphur atom is in +4 oxidation state

- (3) there is a S=S linkage present
(4) each sulphur atom is in identical oxidation state

77. The dipole moment of H_2O_2 is more than that of H_2O but H_2O_2 is not a good solvent because.

- (1) It acts as a reducing agent
(2) It does not acts as an oxidizing agent
(3) It dissociates easily and acts as oxidizing agent in chemical reactions
(4) It has a very high dielectric constant so that ionic compounds cannot be dissolved in it.

Multiple Correct Answers Type

Physical and Chemical Properties

1. Oxygen has -1 oxidation state in the compound

- (1) Caro's acid (2) Marshall's acid
(3) BaO_2 (4) K_2O

2. Oxygen has -2 oxidation state in the compound

- (1) MgO (2) F_2O
(3) Na_2O (4) H_2O_2

3. Select the correct statements about oxygen molecule.

- (1) It is paramagnetic
(2) Its bond order is two
(3) Its liquid state it is colourless
(4) It has two unpaired electrons

4. Which reagent does not give oxygen as one of the products during oxidation with ozone?

- (1) SO_2 (2) $SnCl_2/HCl$
(3) H_2S (4) PbS

5. Which of the following elements form $p\pi-d\pi$ bonding in its oxide?

- (1) Lithium (2) Boron
(3) Sulphur (4) Nitrogen

6. Which of the following statement(s) is/are correct?

- (1) Rhombic sulphur is stable at room temperature
(2) Monoclinic sulphur is stable at room temperature
(3) Both rhombic and monoclinic sulphur has the molecular formula S_8
(4) Both rhombic and monoclinic sulphur are soluble in CS_2

7. Identify the correct statements(s):

- (1) Ozone is a powerful oxidizing agent as compared to O_2
(2) Ozone reacts with KOH and gives an orange coloured solid KO_3
(3) There is a decrease in volume when ozone decomposed to form O_2
(4) The decomposition of O_3 to O_2 is exothermic

8. Which statements are correct for ozone?

- (1) It is obtained by silent electric discharge on oxygen
(2) It can be obtained by the action of ultraviolet rays on oxygen (modified)
(3) It is regarded as an allotrope of oxygen
(4) Ozone molecules is paramagnetic like oxygen molecule

9. Which of the following statements are correct regarding allotropes of Se?
- (1) It shows three grey forms
 - (2) It shows three red non-metallic forms consisting of Se_8 rings
 - (3) The grey metallic forms contains infinite spiral chains of Se atoms with weak metallic interaction between adjacent chains.
 - (4) Grey Se is the only form which conducts electricity
10. Oxygen is evolved when:
- (1) Zinc oxide is treated with NaOH
 - (2) Ammonium nitrate is heated
 - (3) Sodium peroxide reacts with conc. Acid
 - (4) Potassium superoxide reacts with H_2O

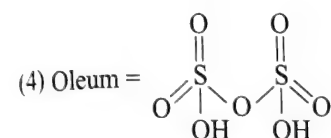
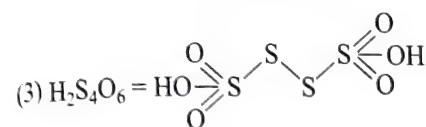
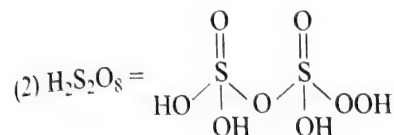
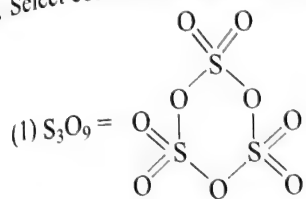
Compounds of Oxygen and Sulphur

11. Solid SeO_3 (selenium trioxide) and TeO_3 exist respectively as
- (1) Cyclic trimer
 - (2) Cyclic tetramer
 - (3) Chain structure
 - (4) Three dimensional net work structure
12. Which among the following are peroxo acid of sulphur?
- (1) H_2SO_3
 - (2) H_2SO_5
 - (3) $\text{H}_2\text{S}_2\text{O}_8$
 - (4) H_2SO_4
13. SO_2 acts as
- (1) Bleaching agent
 - (2) Oxidising agent
 - (3) Reducing agent
 - (4) Dehydrating agent
14. Sulphuric acid can be used as
- (1) Hygroscopic agent
 - (2) Oxidising agent
 - (3) Sulphonating agent
 - (4) Efflorescent
15. SF_6 and SF_4 involves hybridisation of the type _____ and _____ respectively.
- (1) sp^3
 - (2) sp^3d
 - (3) sp^3d^2
 - (4) sp^2
16. Select the correct statements about $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.
- (1) It is also called as hypo
 - (2) It is used in photography to form complex with AgBr
 - (3) It can be used as antichlor
 - (4) It is used to remove stains of I_2
17. Which of the following are amphoteric?
- (1) BeO
 - (2) Al_2O_3
 - (3) ZnO
 - (4) SO_2
18. In which of the following S—S link is present?
- (1) Caro's acid
 - (2) Dithionic acid
 - (3) Thiosulphuric acid
 - (4) Chlorosulphonic acid
19. A yellow coloured crystalline substance gave a colourless gas X on reaction with fluorine, which is thermally stable and has octahedral geometry. X can be
- (1) SF_4
 - (2) S_2F_2
 - (3) SF_6
 - (4) S_2F_6
20. A green coloured solution of a salt changes its colour to light pink on passing ozone through it. Which of the following species represent pink and green colour respectively.
- (1) Mn^{2+} and MnO_2
 - (2) MnO_4^- and MnO_4^{2-}
 - (3) Co^{2+} and Co^{3+}
 - (4) MnO_4^{2-} and MnO_4^-
21. Which concentrated H_2SO_4 can be used to dry the gas?
- (1) H_2S
 - (2) CO_2
 - (3) NH_3
 - (4) All
22. Sulphur on reaction with concentrated HNO_3 gives (A) which reacts with NaOH gives (B). (A) and (B) are
- (1) H_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$
 - (2) NO_2 , Na_2S
 - (3) H_2SO_4 , Na_2SO_4
 - (4) $\text{H}_2\text{S}_2\text{O}_3$, $\text{Na}_2\text{S}_2\text{O}_3$
23. The formation of which of the substance is known as tailing of mercury?
- (1) Hg_2O
 - (2) HgO
 - (3) $\text{Hg}(\text{NO}_3)_2$
 - (4) HgS
24. In which of the following species, S-atom assumes sp^3 hybrid state?
- I (SO_3); II (SO_2); III (H_2S); IV (S_8)
 - (1) I, II
 - (2) II, III
 - (3) II, IV
 - (4) III, IV
25. Which one of the following chemical reactions depicts the oxidising behaviour of H_2SO_4 ?
- (1) $2\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
 - (2) $\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$
 - (3) $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl}$
 - (4) $2\text{PCl}_5 + \text{H}_2\text{SO}_4 \longrightarrow 2\text{POCl}_3 + 2\text{HCl} + \text{SO}_2\text{Cl}_2$
26. Which of the following statements are true about sodium thisoulphate, $\text{Na}_2\text{S}_2\text{O}_3$?
- (1) It contains ionic, covalent and coordinate covalent bonds
 - (2) It is used to remove the unexposed AgBr from photographic films
 - (3) It can give a black precipitate with AgNO_3
 - (4) It is used in the estimation of iodine
27. Which of the following statements are correct about halides of group-16 elements?
- (1) All the elements form hexa-chlorides except oxygen and sulphur
 - (2) Order of thermal stability of the halides of any particular oxidation state decreases in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$
 - (3) Te_2Cl_2 and Po_2Cl_2 are two well known compounds
 - (4) All the elements from hexafluoride except oxygen
28. Peroxy acids of sulphur are:
- (1) $\text{H}_2\text{S}_2\text{O}_3$
 - (2) $\text{H}_2\text{S}_2\text{O}_7$
 - (3) H_2SO_5
 - (4) $\text{H}_2\text{S}_2\text{O}_8$
29. Which of the following statements are correct about tetrahalides?
- (1) The tetra-halides are Lewis bases not Lewis acids
 - (2) $\text{SF}_4 + 2\text{H}_2\text{O} \longrightarrow 4\text{HF} + \text{SO}_2$
 - (3) $\text{SF}_6 + 3\text{H}_2\text{O} \longrightarrow 6\text{HF} + \text{SO}_3$
 - (4) TeCl_4 reacts with HCl to form complex ions such as $[\text{TeCl}_6]^{2-}$

30. Concentrated sulphuric acid is:

- (1) Sulphonating agent (2) Hygroscopic
(3) Oxidizing agent (4) Efflorescent

31. Select correct structures of oxyacid/oxide of sulphur.



32. The reaction of sodium thiosulphate with I_2 gives:

- (1) sodium tetrathionate (2) Sodium sulphate
(3) Sodium iodide (4) Sodium sulphate

33. Sulphur dioxide can be used as:

- (1) Bleaching agent (2) Disinfectant
(3) Antichlor (4) None of these

34. In which of the following reactions conc. H_2SO_4 is used as an oxidizing reagent?

- (1) $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
(2) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$
(3) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
(4) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

35. Consider the following table:

Compound	Enthalpy of formation (kJ mol^{-1})	Bond angle ($H-C, A-H$)	Boiling point ($^{\circ}\text{C}$)
H_2O	x_1	y_1	z_1
H_2S	x_2	y_2	z_2
H_2Se	x_3	y_3	z_3
H_2Te	x_4	y_4	z_4

According to given information the correct order is/are:

- (1) $x_1 > x_2 > x_3 > x_4$ (2) $y_1 > y_2 > y_3 > y_4$
(3) $z_1 > z_2 > z_3 > z_4$ (4) $x_1 > x_4 > x_3 > x_2$

36. Which of the following orders represents the correct order for the properties indicated against them?

- (1) $H_2S < H_2Se < H_2Te$ (covalent character)
(2) $H_2S > H_2Se > H_2Te$ (thermal stability)
(3) $H_2S > H_2Se > H_2Te$ (reducing nature)
(4) $H_2S < H_2Se < H_2Te$ (acidic character)

37. Which of the following statements are correct?

- (1) Change in enthalpy is positive for the preparation of SO_3 by catalytic oxidation of SO_2

- (2) Iron powder along with Al_2O_3 and K_2O is used as a catalyst in the preparation of NH_3 by Haber's process
(3) In peroxosulphuric acid (H_2SO_5) sulphur is in oxidation state
(4) S-S bond is present in $H_2S_2O_6$

38. Select the correct statements.

- (1) $ZnO > Ga_2O_3 > Al_2O_3 > BeO$ (amphoteric oxides)
(2) Na_2O behaves both as basic and as well as normal oxide
(3) Hg_2O dissolves in Hg which loses its meniscus and stick to glass (tailing of mercury), is represented by the reaction
 $O_3 + 2H^+ + 2H_{2(g)} \longrightarrow O_2 + H_2O + Hg_2^{2+}$
(4) During the oxidation of $SnCl_2$ to $SnCl_4$ by O_3 , O_2 is evolved.

39. Which of the following parent acid(s) does not have corresponding hypo-oxyacid?

- (1) HNO_3 (2) $HClO_3$
(3) H_3PO_4 (4) H_2SO_4

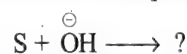
40. Oxyanion (S) containing (6, 2) pair of equivalent X-O linkage (where X-central atom) is/are:

- (1) $P_2O_6^{4-}$ (2) $P_2O_8^{4-}$
(3) $P_2O_7^{4-}$ (4) $S_2O_8^{2-}$

41. Select the correct statement(s)

- (1) NO and ClO_2 both have fractional bond order.
(2) NO and ClO_2 both have odd e^- bond in their structures and both are paramagnetic.
(3) SF_4 is hydrolyzed by H_2O to give H_2SO_3 and HF as final product.
(4) During hydrolysis of SF_4 , S-atom in transition state is sp^3d^2 hybridized.

42. What are the products in the following reaction?



- (1) S^{2-} (2) SO_3^{2-}
(3) S_5^{2-} (4) $S_2O_3^{2-}$

43. Select the correct statement about O_3 ?

- (1) O_3 oxidises $[Fe(CN)_6]^{3-}$
(2) Moist I_2 reacts with O_3 to give I_2O_5
(3) O_3 acts as mild bleaching agent but cannot act as a bleaching agent in dry state
(4) O_3 oxidises I^{\ominus} , AsO_3^{3-} and MnO_4^{2-}

44. Select the correct statements:

- (1) Solid O_2 is blue, liquid O_2 is pale blue, and gaseous O_2 is colourless.
(2) O_2 loses its paramagnetic character when it is cooled below a reaction temperature.
(3) O_2 does not react with, Zn, Ti and Fe directly.
(4) O_3 destroys mercury meniscus and is used in swimming pools.

45. Select the correct statements

- (1) Monoclinic sulphur melts to clear mobile liquid at 119°C
(2) Monoclinic sulphur on heating from 160 to 190°C , it becomes viscous

- (3) Monoclinic sulphur on heating upto 200°C , the viscosity decreases
- (4) Dry SO_2 bleach dry flowers
46. Select the correct statements about the contact process for the manufacture of H_2SO_4
- (1) Low temperature for the conversion of SO_2 to SO_3 is required, as the reaction is exothermic (720 K)
- (2) High pressure (2 atm.) is required for the conversion of SO_2 to SO_3 which decreases in volume
- (3) In contact process, SO_3 is not absorbed directly in H_2O to form H_2SO_4 because the reaction is highly exothermic, acid mist is formed. Hence the reaction becomes difficult to handle
- (4) A catalyst (Pt or V_2O_5) is required to increase the yield of the reaction.

Linked Comprehension Type

Paragraph 1

H_2SO_4 is the most important acid used in the chemical industry. Concentrated H_2SO_4 has quite strong oxidising properties.

- H_2SO_4 acts as
 - Reducing agent
 - Oxidising agent
 - Only monobasic acid
 - None of these
- The shape of H_2SO_4 is
 - Tetrahedral
 - Pyramidal
 - Planar
 - T-shaped
- Oxidation state of S in H_2SO_4 is
 - +6
 - +4
 - +2
 - +3

Paragraph 2

Hydrogen peroxide is an important compound of hydrogen and oxygen. It shows various types of properties and chemical reactions.

- Hydrogen peroxide is not
 - A reducing agent
 - An oxidising agent
 - A dehydrating agent
 - A bleaching agent
- The reaction $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \longrightarrow \text{S} + 2\text{H}_2\text{O}$ manifests
 - Acidic nature of H_2O_2
 - Alkaline nature of H_2O_2
 - Oxidising action of H_2O_2
 - Reducing nature of H_2O_2
- The species that do not contain peroxide ion (s) is/are
 - PbO_2
 - SrO_2
 - Na_2O_2
 - BaO_2
- The oxidation state of oxygen in H_2O_2 is
 - +1
 - 1
 - +2
 - 2

Paragraph 3

Sulphuric acid is considered as the king of chemicals. The prosperity of any country is measured by the amount of sulphuric acid it consumes. Sulphuric acid is, thus, a substance of very great commercial importance as it is used practically in every important industry. This is due to the following properties of sulphuric acid:

- acidic nature
 - oxidising nature
 - dehydrating nature
 - sulphonation
8. Sulphuric acid has very corrosive action on skin because
- It reacts with proteins
 - It acts as an oxidising agent
 - It acts as a dehydrating agent
 - It acts as a dehydrating agent and absorption of water is highly exothermic
9. Which of the following reactions depict the oxidising behaviour of H_2SO_4 ?
- $2\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
 - $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl}$
 - $2\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
 - $2\text{PCl}_5 + \text{H}_2\text{SO}_4 \longrightarrow 2\text{POCl}_3 + 2\text{HCl} + \text{SO}_2\text{Cl}_2$
10. Sulphuric acid is used
- In lead storage batteries
 - In making fertilizers
 - In making explosives
 - All of these
11. Concentrated H_2SO_4 cannot be used to prepare HBr or HI from KBr or KI because it
- Reacts too slowly with KBr or KI
 - Reduces HBr or HI
 - Oxidises HBr or HI
 - Oxidises KBr to KBrO_3 or KI to KIO_3
12. Only carbon is obtained when concentrated H_2SO_4 is added to
- Formic acid
 - Cane sugar
 - Oxalic acid
 - Ethyl alcohol
13. The formation of nitroglycerine is done by the use of concentrated nitric acid and concentrated sulphuric acid. The process of conversion of glycerine into nitroglycerine is termed as
- Sulphonation
 - Oxidation
 - Nitration
 - Dehydration

Paragraph 4

The binary compounds of oxygen with other elements are called oxides. They are classified depending either upon their acid-base characteristics or on the basis of oxygen content.

- Normal oxides:** These oxides which contain oxygen atoms as permitted by the normal oxidation number, i.e., -2 normal oxide may be acidic, basic, amphoteric or neutral.
- Polyoxides:** The oxides which contain oxygen atoms different than those permitted by the normal oxidation number of -2.
 - Peroxides:** Two oxygen atoms are linked to each other and each oxygen has -1 oxidation number. They contain $(\text{O} - \text{O})^{2-}$ unit.
 - Superoxides:** These oxides contain $(\text{O} - \text{O})^{-1}$ unit, i.e., each O-atom has oxidation number -1/2.
- Suboxides:** These contain low content of oxygen than expected.
- Mixed oxides:** These oxides are made of two simpler oxides.

14. Which pair of species is referred to as suboxides?
 (1) CO, NO (2) SO₂, CaO
 (3) N₂O, CO (4) N₂O, C₃O₂
15. Which of the following pairs contains neutral oxides?
 (1) SO₂, SO₃ (2) N₂O₃, N₂O₅
 (3) CO, NO (4) Na₂O, CaO
16. Which of the following pairs contains mixed oxides?
 (1) Pb₃O₄, Fe₃O₄ (2) MnO₂, BaO₂
 (3) KO₂, Na₂O₂ (4) Mn₃O₄, N₂O₅
17. Which of the following pairs contains amphoteric oxides?
 (1) BeO, BaO (2) BeO, Al₂O₃
 (3) Al₂O₃, P₂O₅ (4) FeO, CuO
18. Which of the following oxides is paramagnetic in nature?
 (1) KO₂ (2) BaO₂
 (3) H₂O (4) CO₂

Paragraph 5

Sulphur and rest of the elements of group 16 are less electronegative than oxygen. Therefore, their atoms cannot take electrons easily. They can acquire ns^2np^6 configuration by sharing two electrons with the atoms of other elements and thus, exhibit +2 oxidation state in their compounds. In addition to this, their atoms have vacant d -orbitals in their valence shell to which electrons can be promoted from the p and s -orbitals of the same shell. As a result, they can show +4 and +6 oxidation states.

19. The oxidation state of sulphur in S₈, SO₃ and H₂S respectively are
 (1) 0, +6, -2 (2) +2, +6, -2
 (3) 0, +4 +2 (4) -2, +6, +2
20. The oxidation state of sulphur in Na₂S₄O₆ is
 (1) 2/3 (2) 3/2
 (3) 3/5 (4) 5/2
21. The nature of the compounds of sulphur having +4 oxidation state is
 (1) Act as oxidising agents
 (2) Act as reducing agents
 (3) Act as oxidising as well as reducing agents
 (4) Cannot be predicted
22. Like sulphur, oxygen does not show +4 and +6 oxidation states. The reason is
 (1) That oxygen is a gas while sulphur is a solid
 (2) That oxygen has high ionisation enthalpies in comparison to sulphur
 (3) That oxygen has high electron affinity in comparison to sulphur
 (4) That oxygen has no d -orbitals in its valence shell
23. Oxygen exhibits +2 oxidation state in
 (1) H₂O (2) OF₂
 (3) Cl₂O (4) H₂O₂

Matching Column Type

This section contains questions each with two columns I and II. Match the items given in column I with that in column II.

Column I	Column II
a. SOF ₂	p. Oxyacid formed during hydrolysis undergo tautomeric change
b. H ₂ S ₂ O ₈	q. Oxidation state of central atom does not change during hydrolysis
c. XeOF ₄	r. Both partial and complete hydrolysis is possible
d. POCl ₃	s. Hydrolyzed product reacts with glass
	t. Hybridization of central atom in the final product-remains same as in the substrate on hydrolysis

Column I	Column II
a. $\text{H}_2\text{S}_2\text{O}_8 \xrightarrow{\text{H}_2\text{O}}$	p. Dibasic acid
b. $\text{SF}_4 \xrightarrow{\text{H}_2\text{O}}$	q. Can act as flexidentate ligand
c. $\text{NCl}_3 \xrightarrow{\text{H}_2\text{O}}$	r. Can act as both oxidizing and reducing agent
d. $\text{NO}_2 \xrightarrow{\text{H}_2\text{O}}$	s. Can act as mono-dentate ligand
	t. Non-redox hydrolysis

Column I (Property of SO ₂)	Column II (Reaction)
a. Acidic nature	p. $2\text{Mg} + \text{SO}_2 \rightarrow 2\text{MgO} + \text{S}$
b. Oxidising nature	q. $\text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_3$
c. Reducing nature	r. $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$
d. Non-supporter of combustion	s. $\text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ + 3\text{SO}_2 \rightarrow 3\text{SO}_4^{2-} + \text{H}_2\text{O} + 2\text{Cr}^{3+}$

Column I	Column II
a. Oil of vitriol	p. H ₂ S ₂ O ₇
b. Fuming H ₂ SO ₄	q. H ₂ SO ₅
c. Oleum	r. H ₂ SO ₄
d. Caro's acid	s. SO ₃ + H ₂ SO ₄

Column I (Compound of S)	Column II (Hybridisation of S)
a. SF ₆	i. sp^3d
b. SO ₂	ii. sp^3
c. SCl ₄	iii. sp^2
d. H ₂ SO ₄	iv. sp^3d^2

6.	Column I (Allotropic form)	Column II (Structure)
a.	Engel's sulphur	p. Rings, chair conformation, stable
b.	Sulphur	q. Fibrous or rubber like

c.	Rhombic sulphur	r.	Crystalline form, yellow crystals
d.	Monoclinic sulphur	s.	Puckered S_8 rings, crown conformation

7. Match the items given in Column I with that in Column II and III.

Column I	Column II	Column III
Oxides	Compounds	Characteristics
a. Superoxides	i. C_3O_2	p. React with water to give H_2O_2 and O_2
b. Peroxides	ii. CsO_2	q. React with dil. H_2SO_4 to give H_2O_2 and with conc. H_2SO_4 to give $H_2O_2 + O_2$
c. Suboxides	iii. N_2O	r. Contains $3\bar{e}$ bonds and are paramagnetic and coloured
d. Neutral oxide	iv. BaO_2	s. They involve M-M bonds in addition to M-O bonds

8. Match the items given in Column I with that in Column II and III.

Column I	Column II	Column III
Characteristics (I)	Characteristics (II)	Compound
a. In Solid State it exists as a cyclic trimer or a linear polymeric chain structure.	i. Element is used for photocopying (Xerox). It is also used as a decolouriser of glass	p. O_2
b. In solid state it exists as cyclic tetramer structure	ii. Trigangular planar gaseous molecule at room temperature. sp^2 hybridised, with 2 ($p\pi - d\pi$) bond	q. SeO_3
c. Pale blue gas and is diamagnetic	iii. Used in Ostwall process	r. SO_3
d. It oxidises NH_3 to $NO(g)$ in presence of Pt gauge as catalyst at 1100 K	iv. The gas reacts with Hg and Hg_2O is formed which dissolves in Hg, which loses its meniscus and sticks to glass. It is called tailing of mercury	s. O_3

9. Match the items given in Column I with that in Column II and III.

Column I	Column II	Column III
Oxo-acids of phosphorous	Characteristics (I)	Characteristics (II)
a. Phosphinic acid	i. Dibasic, (+3) O.S., 2(P-OH), 1(P-H), and 1(P=O) bond	p. $P_4 + 3NaOH \longrightarrow PH_3 + 3H_2O + \dots$
b. Phosphonic acid	ii. Tribasic, (+5) O.S. 2(P-OH), 1(P=O) and 1(P-O-O-H) bond	q. $2H_3PO_4 \xrightarrow{520\text{ K}} H_4P_2O_7 \xrightarrow{870\text{ K}} \dots$
c. Metaphosphoric acid	iii. Monobasic, (+1) O.S. 1(P-OH), 2(P-H) and 1(P=O) bond	r. $PCl_3 + 3H_2O \longrightarrow 3HCl + \dots$
d. Per mono-oxo-phosphoric acid	iv. Monobasic (+5) O.S. 1(P-OH) and 2(P=O) bond. Exists in polymeric form	s. $P_4O_{10} + 4H_2O_2 (30\%) + 2H_2O \longrightarrow \dots$
		t. Strongest reducing agent

Numerical Value Type

- What is oxidation state of sulphur in Caro's acid?
- How many π -bonds are present in Marshall's acid?
- Ozone reacts with dry iodine to form an oxide having _____ oxygen atoms in its molecules.
- How many S-S bonds are present in S_8 molecule?
- Among the oxides given below, how many are acidic?
 CrO_3 , Mn_2O_7 , CuO , CO , SO_2

- In how many of the following species, S-atom is sp^3 hybridised?
 S_8 , SO_4^{2-} , SO_3 , H_2S , SCl_4
- What is the number of σ bonds present in peroxodisulphuric acid?
- Conc. H_2SO_4 reacts with four moles of Ag to give _____ moles of Ag_2SO_4 .
- If P represent total number of lone pairs (non bonding electron pairs)

Q represent total number of π -bonds.

R represents total number of σ -bonds

Then calculate the value $(P + Q - R)$ in pentathionic acid.

10. If P , Q and R are total number of $(p\pi-d\pi)$ bonds in (i) $H_2S_2O_5$ (ii) $H_2S_2O_6$ and (iii) H_2SO_3 then calculate the value of $(P + Q + R)$.

11. If P represents sp^3 -hybridised atoms

Q represents sp^2 -hybridised atoms.

R represents number of $(p\pi-d\pi)$ bonds.

Then calculate the value of $(P + R - Q)$ in Marshall's acid.

Archives

JEE MAIN

Single Correct Answer Type

1. Which of the following statements regarding sulphur is incorrect?

- (1) S_2 molecule is paramagnetic
- (2) The vapor at 200°C consists mostly of S_8 rings
- (3) At 600°C , the gas mainly consists of S_2 molecules
- (4) The oxidation state of sulphur is never less than +4 in its compounds

(AIEEE 2011)

2. The products obtained on heating $LiNO_3$ will be

- (1) $LiNO_2 + O_2$
- (2) $Li_2O + NO_2 + O_2$
- (3) $Li_3N + O_2$
- (4) $Li_2O + OH + O_2$

(AIEEE 2011)

3. Which of the following is wrong statement?

- (1) $ONCl$ and ONO^- are not isoelectronic
- (2) O_3 molecule is linear
- (3) Ozone is violet-black in solid state
- (4) Ozone is diamagnetic gas

(JEE Main 2013)

JEE ADVANCED

Single Correct Answer Type

1. The number of S—S bonds in sulphur trioxide trimer (S_3O_9) is

- (1) three
- (2) two
- (3) one
- (4) zero

(IIT-JEE 2001)

2. Which of the following is not oxidised by O_3 ?

- (1) KI
- (2) $FeSO_4$
- (3) $KMnO_4$
- (4) K_2MnO_4

(IIT-JEE 2005)

3. The species having pyramidal shape is

- (1) SO_3
- (2) BrF_3
- (3) SiO_3^{2-}
- (4) OSF_2

(IIT-JEE 2010)

4. Which of the following does not give oxygen on heating?

- (1) $K_2Cr_2O_7$
- (2) $(NH_4)_2Cr_2O_7$
- (3) $KClO_3$
- (4) $Zn(ClO_3)_2$

(JEE Advanced 2013)

Multiple Correct Answers Type

1. The pair(s) of reagents that yield paramagnetic species is /are

- (1) Na and excess of NH_3
- (2) K and excess of O_2
- (3) Cu and dilute HNO_3
- (4) O_2 and 2-ethylantraquinol

(JEE Advanced 2014)

Numerical Value Type

1. Among the following, how many elements show only one non-zero oxidation state?

O, Cl, F, N, P, Sn, Tl, Na, Ti

(IIT-JEE 2010)

2. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is

(IIT-JEE 2010)

3. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue.

KCN , K_2SO_4 , $(NH_4)_2C_2O_4$, $NaCl$, $Zn(NO_3)_2$, $FeCl_3$, K_2CO_3 , NH_4NO_3 , $LiCN$.

(IIT-JEE 2010)

4. The difference in the oxidation number of two types of S-atoms in $Na_2S_4O_6$ is

(IIT-JEE 2011)

5. A list of species having the formula XZ_4 is given below:

XeF_4 , SF_4 , SiF_4 , BF_4^- , $[Cu(NH_3)_4]^{2+}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$.

Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

(JEE Advanced 2014)

Answers Key

EXERCISES

Single Correct Answer Type

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (2) | 2. (1) | 3. (4) | 4. (2) | 5. (4) |
| 6. (4) | 7. (3) | 8. (3) | 9. (3) | 10. (2) |
| 11. (2) | 12. (3) | 13. (4) | 14. (4) | 15. (3) |
| 16. (3) | 17. (1) | 18. (3) | 19. (1) | 20. (1) |
| 21. (1) | 22. (3) | 23. (2) | 24. (2) | 25. (3) |
| 26. (4) | 27. (1) | 28. (2) | 29. (1) | 30. (4) |
| 31. (2) | 32. (4) | 33. (1) | 34. (2) | 35. (3) |
| 36. (2) | 37. (2) | 38. (3) | 39. (4) | 40. (2) |
| 41. (1) | 42. (1) | 43. (2) | 44. (3) | 45. (4) |
| 46. (1) | 47. (4) | 48. (2) | 49. (4) | 50. (1) |
| 51. (2) | 52. (3) | 53. (3) | 54. (2) | 55. (3) |
| 56. (4) | 57. (1) | 58. (4) | 59. (2) | 60. (1) |
| 61. (2) | 62. (3) | 63. (3) | 64. (1) | 65. (2) |
| 66. (3) | 67. (2) | 68. (3) | 69. (4) | 70. (1) |
| 71. (3) | 72. (1) | 73. (1) | 74. (1) | 75. (4) |
| 76. (3) | 77. (3) | | | |

Multiple Correct Answers Type

- | | | |
|------------------|------------------|---------------|
| 1. (1, 2, 3) | 2. (1, 3) | 3. (1, 2, 4) |
| 4. (1, 2) | 5. (3) | 6. (1, 3, 4) |
| 7. (1, 2, 4) | 8. (1, 2, 3) | 9. (2, 3, 4) |
| 10. (3, 4) | 11. (2, 4) | 12. (2, 3) |
| 13. (1, 2, 3) | 14. (1, 2, 3) | 15. (2, 3) |
| 16. (1, 2, 3, 4) | 17. (1, 2, 3) | 18. (2, 3) |
| 19. (3) | 20. (4) | 21. (2) |
| 22. (3) | 23. (1) | 24. (4) |
| 25. (1) | 26. (2, 3, 4) | 27. (1) |
| 28. (2, 4) | 29. (1, 4) | 30. (1, 2, 3) |
| 31. (1, 3, 4) | 32. (1, 3) | 33. (1, 2, 3) |
| 34. (2, 3) | 35. (1, 2, 3) | 36. (1, 2, 4) |
| 37. (3, 4) | 38. (2, 3) | 39. (1, 2) |
| 40. (2, 3, 4) | 41. (1, 2, 3, 4) | 42. (1, 3, 4) |
| 43. (3, 4) | 44. (1, 2, 4) | 45. (1, 2, 3) |
| 46. (1, 2, 3) | | |

Linked Comprehension Type

- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (2) | 2. (1) | 3. (1) | 4. (3) | 5. (1) |
| 6. (1) | 7. (2) | 8. (4) | 9. (1) | 10. (4) |

- | | | | | |
|---------|---------|---------|---------|---------|
| 11. (3) | 12. (2) | 13. (3) | 14. (4) | 15. (3) |
| 16. (1) | 17. (2) | 18. (1) | 19. (1) | 20. (4) |
| 21. (3) | 22. (4) | 23. (2) | | |

Matching Column Type

Q.No.	a.	b.	c.	d.
1.	q	r	s	p
2.	s	r	q	p
3.	q	r	s	p
4.	r	s	p	q
5.	s	r	p	q
6.	p	s	r	q
7.	ii-p,r	iv-q	i, iii-s	iii-s
8.	ii-r	i-q	iv-s	iii-p
9.	iii-p,t	i-r	iv-q	ii-s

Numerical Value Type

- | | | | | |
|-----------|--------|--------|---------|---------|
| 1. (6) | 2. (4) | 3. (9) | 4. (8) | 5. (3) |
| 6. (3) | 7. (9) | 8. (2) | 9. (10) | 10. (8) |
| 11. (1.2) | | | | |

ARCHIVES

JEE Main

Single Correct Answer Type

- | | | |
|--------|--------|--------|
| 1. (4) | 2. (2) | 3. (2) |
|--------|--------|--------|

JEE Advanced

Single Correct Answer Type

- | | | | |
|--------|--------|--------|--------|
| 1. (4) | 2. (3) | 3. (4) | 4. (2) |
|--------|--------|--------|--------|

Multiple Correct Answers Type

- | |
|--------------|
| 1. (1, 2, 3) |
|--------------|

Numerical Value Type

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (2) | 2. (3) | 3. (3) | 4. (5) | 5. (4) |
|--------|--------|--------|--------|--------|

4

p-Block Group 17 Elements The Halogen Family

OVERVIEW

1. Group 17 of the periodic table consists of fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Collectively, these elements are also known as halogens (Greek: 'halo' meaning 'salt' and 'genes' meaning 'born' or 'salt producer').

2. General electronic configuration of halogens is ns^2np^5 , i.e. they are just short of one electron to attain the stable electronic configuration of the next noble gas.

3. Due to their high reactivity, halogens are never found in free state, but in the combined state. Fluorine is known as 'super halogen'.

4. All halogens exist as diatomic molecules, X_2 . At room temperature, F_2 and Cl_2 are gases, Br_2 is liquid and I_2 is solid. Weak van der Waals forces of attraction hold the diatomic molecules together, and as these forces increase with molecular mass, nature of halogens changes from gas \rightarrow liquid \rightarrow solid.

5. i. Atomic radii: $F < Cl < Br < I$

ii. Melting point: $F_2 < Cl_2 < Br_2 < I_2$

iii. Boiling point: $F_2 < Cl_2 < Br_2 < I_2$

6. Halogens have high ionisation enthalpies. Ionisation enthalpy: $F < Cl < Br < I$.

Iodine forms positive ion, I^+ , i.e. shows metallic character, non-metallic character decreases from F to I.

7. All the halogens are coloured, due to absorption of some wavelength of visible light by their molecules to cause $\pi^* \rightarrow \sigma^*$ transition.

F_2	Cl_2	Br_2	I_2
Yellowish green	Greenish yellow	Brownish red	Violet

8. Electronegativity: $F > Cl > Br > I$

Fluorine is the highest electronegative element of the periodic table.

9. Electron affinity: $F < Cl > Br > I$

F has less electron affinity than Cl due to high repulsion between the electron to be added and the electrons already present in F (due to small size of F).

10. Bond length: $F_2 < Cl_2 < Br_2 < I_2$

Despite the fact that bond length of $F_2 < Cl_2$, bond dissociation enthalpy of F_2 is less than Cl_2 . This is due to high lp-lp repulsion between the electrons present in F-F.

11. Fluorine shows an oxidation state of -1 only, except in HOF, where its oxidation state is +1.

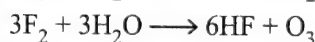
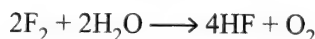
Cl, Br and I show -1, +1, +3, +5 and +7 oxidation states. Due to presence of vacant *d*-orbitals in Cl, Br and I, higher oxidation states are possible. In oxides and oxyacids, +4 and +6 oxidation states are also shown.

12. Standard reductive potentials of halogens are positive and decrease from F to I. Thus halogens act as strong oxidising agents.

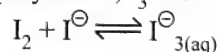
Oxidising power: $F_2 > Cl_2 > Br_2 > I_2$

13. F^\ominus ion does not show any reducing nature, but Cl^\ominus , Br^\ominus and I^\ominus act as reducing agent.

14. **With water:** Fluorine reacts with water even in dark, producing O_2 and O_3 .



Cl_2 and Br_2 are fairly soluble in water and form chlorine water and bromine water. I_2 does not dissolve in water. I_2 is more soluble in KI solution than in pure water, due to formation of polyhalide, I_3^\ominus ion.



On careful evaporation of Cl_2 water or Br_2 water, crystals of composition $Cl_2 \cdot 8H_2O$ and $Br_2 \cdot 8H_2O$ are formed.

15. Aqueous solution I_2 is brown in colour while organic solutions of I_2 are violet in colour.

16. I_2 is used in medicine in the form of tincture of iodine (2-3% alcoholic solution of I_2) and iodex ointment (consists of I_2 and methyl salicylate in a vaseline base).

17. NaBr and KBr are used as sedatives.

18. With hydrogen, all the halogens form volatile covalent hydrides, HX. These hydrides are known as halogen acids or hydracids.

HF is a liquid due to association of molecules through hydrogen bonding.

i. Boiling point : $HF > HCl > HBr > HI$

ii. Bond strength : $HF > HCl > HBr > HI$

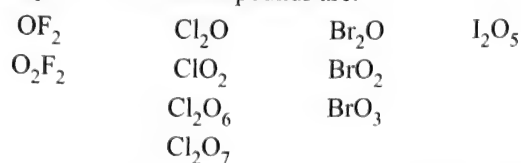
iii. Bond dissociation enthalpy: $HF > HCl > HBr > HI$

iv. Reducing nature : $HF < HCl < HBr < HI$

(HF does not show reducing nature)

v. Dipole moment (μ) : $HF > HCl > HBr > HI$

19. Halogens and oxygen do not combine directly with each other. However, these compounds have been obtained indirectly. The known compounds are:



The compounds of oxygen and fluorine are not called oxides but fluorides as fluorine is more electronegative than oxygen.

- Oxides of Cl, Br and I are acidic and acidic character increases with increase of percentage of oxygen in them.
 - All the oxides of halogens are powerful oxidants, highly reactive and unstable towards heat. In general, higher oxides are relatively more stable than lower oxides for a particular halogen.
 - Oxygen fluorides do not form oxyacids.
 - In these oxides, bonds are mainly covalent due to small difference in the electronegativity of oxygen and halogens.
 - All the three monoxides, viz., OF₂, Cl₂O and Br₂O have tetrahedral geometry involving sp^3 hybridisation of oxygen, bond angle increases with increase in size of the halogen atom.
 - Oxides of iodine I₂O₄ and I₄O₉ are not true oxides but iodates, IO(IO₃) and I(IO₃)₃ respectively.
20. Except fluorine, all other halogens form oxyacids of the type HOX, HXO₂, HXO₃ and HXO₄. Some of these acids are quite unstable.

Cl	Br	I	
HOCl	HOBr	HOI	Hypohalous
HClO ₂	—	—	Halous
HClO ₃	HBrO ₃	HIO ₃	Halic
HClO ₄	HBrO ₄	HIO ₄	Perhalic

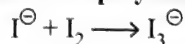
- All these acids are monobasic and the halogen atom is sp^3 hybridised.
 - Acidic character increases with increase in oxidation number of the halogen.
 $\text{HOCl} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
 - In any series, acidic character decreases as the electronegativity decreases.
 $\text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$
 - Oxidising nature for the same halogen decreases.
 $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$
 - Stability for the same halogen increases.
 $\text{HOCl} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
21. The important minerals of fluorine are:
(i) Fluorspar (CaF₂); (ii) Cryolite (Na₃AlF₆);
(iii) Fluorapatite [CaF₂·3Ca₃(PO₄)₂]
In small amounts, it is present as fluorides in plant ashes, soil, sea water, bones and teeth of animals.
Fluorine was discovered by **Joseph Henri Moissan** in 1886.
22. The fluorine compounds have wide applications:
- Freon, CF₂Cl₂ (dichlorodifluoro methane) is used in refrigerants and cold storage plants.

- Teflon (C₂F₄), a new plastic, has a very high electrical resistance and is used as insulating material. It is not affected by acids, alkalies and strong oxidising agents.
 - H₂F₂ is used for etching of glass.
 - SF₆ has insulating properties. It is used in X-ray and high voltage machines.
 - NaF and Na₃AlF₆ are used as insecticides.
 - CuF₂ is used in ceramic industry.
 - UF₆ is used for separation of ²³⁵U isotope from natural uranium.
 - Sodium fluoroacetate is used as a rat poison.
23. Chlorine was discovered by **Scheele** in 1774. The old name is oxymuriatic acid gas. Common salt (NaCl) is the most important chloride which occurs in sea water, lakes and in rocks.
24. Chlorine is a yellowish green gas with pungent suffocation and poisonous nature. It is fairly soluble in water. The aqueous solution is called chlorine water which gives crystal of chlorine hydrate (Cl₂·8H₂O) at 0°C. In presence of moisture it acts as an oxidising and bleaching agent.
25. Chlorine is used in the manufacture of bleaching powder, chlorates, hypochlorites, HCl, chloroform, CCl₄, phosgene (COCl₂), tear gas (CCl₃NO₂) and mustard gas (Cl—C₂H₄—S—C₂H₄—Cl). It is used in the purification of drinking water and as a bleaching agent for cotton fabrics, paper and rayon.
26. Bromine was discovered by **Balard** in 1826. It is obtained either from the mother liquor (called *bittern*) obtained after crystallising KCl from carnallite or from sea water by passing Cl₂ gas. The vapours are absorbed in Na₂CO₃ solution when a mixture of NaBr and NaBrO₃ is obtained which is distilled with H₂SO₄ to recover bromine.
27. Iodine was discovered by **Courtois** in 1812. Two main sources of iodine are:
- Deep sea-weeds ashes known as kelp which contains 0.5% iodine in the form of iodides.
 - Caliche or crude chile saltpetre which contains 0.2% of NaIO₃.
28. I₂ is slightly soluble in water. The solubility can be increased by addition of KI.
- $$\text{KI} + \text{I}_2 \longrightarrow \text{KI}_3 \text{ (Soluble)}$$
- It is soluble in organic solvents such as chloroform, carbon tetrachloride, alcohol, ether, etc. It oxidises Na₂S₂O₃ into sodium tetrathionate. This reaction is useful in iodometric titrations.
29. The halogens on account of difference in the electronegativities combine with each other to form compounds of the type AX_n, where A is always a bigger atom and X is a smaller atom and *n* may have values 1, 3, 5 and 7. These are covalent compounds called **interhalogen compounds**.
- AX type ClF, BrF, BrCl, ICl, IBr $\longrightarrow sp^3d$ hybridisation of A, three lone pairs.
- AX₃ type ClF₃, BrF₃, ICl₃ $\longrightarrow sp^3d$ hybridisation of A, two lone pairs.
- AX₅ type IF₅, BrF₅ $\longrightarrow sp^3d^2$ hybridisation of A, one lone pair.

AX_7 type $IF_7 \rightarrow sp^3d^3$ hybridisation of A.

Interhalogen compounds are gases or liquids. These are volatile and fume in air. These compounds are more reactive than halogens except fluorine because A—B bond is weaker than A—A and B—B bond. These are hydrolysed and act as oxidising agents.

30. Halide ions often react with molecules of halogens or interhalogens and form **polyhalides**.



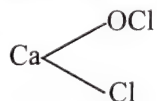
I_3^- (polyhalide) ion is stable in aqueous solution and in ionic crystals. More complex ions such as I_5^- , I_7^- and I_9^- have been prepared. The Br_3^- and Cl_3^- ions are much less stable than I_3^- .

Many polyhalides are known in which two or three different halogens are present such as ICl_2^- , ICl_4^- , $(IBrF)^-$ and $(IBrCl)^-$.

31. Some of the monovalent ions made of electronegative atoms possessing properties similar to halide ions are known as **pseudohalide ions**. The corresponding dimers having no charge of these pseudohalide ions are called pseudohalogens.

Pseudohalide ions	Pseudohalogens
Cyanide ion (CN^-)	$(CN)_2$ Cyanogen
Thiocyanate ion (SCN^-)	$(SCN)_2$ Thiocyanogen
Cyanate ion (OCN^-)	$(OCN)_2$ Oxycyanogen

32. Bleaching powder ($CaOCl_2 \cdot H_2O$) is also called calcium chlorohypochlorite because it is a mixed salt of hydrochloric acid and hypochlorous acid. It is represented as



It is obtained by the action of Cl_2 on slaked lime.

Bleaching powder loses its chlorine content by the action of dilute acids or carbon dioxide. The amount of chlorine obtained from the sample of a bleaching powder by this way is termed available chlorine. A good sample of bleaching

powder contains 35–38% of available chlorine.

On long standing bleaching powder undergoes auto-oxidation into calcium chlorate and calcium chloride.



The products do not have available chlorine.

Thus, bleaching powder loses available chlorine with time.

33. When a chloride is heated with conc. H_2SO_4 in presence of solid $K_2Cr_2O_7$ in a dry test tube, deep red vapours of chromyl chloride are evolved. When these vapours are passed through NaOH solution, the solution becomes yellow due to formation of sodium chromate. The solution is neutralised with acetic acid and on addition of lead acetate solution, a yellow precipitate of lead chromate is formed. This is a test of chloride ion and is known as chromyl chloride test.
34. Warming $KClO_3$ with conc. HCl gives a mixture of Cl_2 and ClO_2 known as euchlorine which is a bleaching agent.
35. Iodine shows an electropositive nature as it has the lowest ionisation potential among halogens. It has the tendency to lose electron or electrons to form I^+ and I^{3+} cations. Compounds such as ICl_3 , ICN , ICl_3 , IPO_4 , $I(CH_3COO)_3$, etc., are known.
36. Some of the products of halogens have been given special names.
- | | |
|----------------------------|------------------------|
| $Mg(ClO_4)_2$ | — Anhydron |
| $KClO_3$ | — Berthelot's salt |
| KHF_2 | — Ferming's salt |
| Aq. soln. of NaOCl | — Javelle water |
| $CaOCl_2 \cdot H_2O$ | — Bleaching powder |
| Cl_2 and ClO_2 mixture | — Euchlorine |
| Soln. of HCl | — Spirit of salt |
| $CCl_3 \cdot NO_2$ | — Tear gas |
| Cl_2 | — Oxymuriatic acid gas |
37. Cl_2 and F_2 do not react with starch solution. Br_2 gives yellow colour with starch solution and I_2 gives deep blue colour with starch solution.

Some Examples of Hybridisation of Group 17 ($7e^-$)

1. Interhalogen compounds:

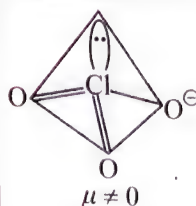
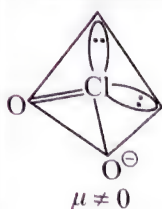
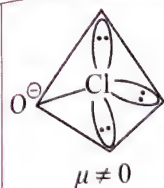
$:\ddot{\text{I}}-\text{F}$	$:\ddot{\text{I}}\text{F}_3$	$:\text{IF}_5$	IF_7
Iodine fluoride sp^3 hybridisation with 3lp $\text{SN} = 1 \text{ bp} + 3 \text{ lp} = 4$	Iodine trifluoride sp^3d hybridisation with 2lp $\text{SN} = 3 \text{ bp} + 2 \text{ lp} = 5$	Iodine pentafluoride sp^3d^2 hybridisation with 1lp $\text{SN} = 5 \text{ bp} + 1 \text{ lp} = 6$	Iodine heptafluoride sp^3d^3 $\text{SN} = 7 \text{ bp}$
$\text{H} = sp^3$ $\text{G} = \text{Tetrahedral}$ $\text{Shape} = \text{Linear}$	$\text{H} = sp^3d$ $\text{G} = \text{Trigonal bipyramidal}$ $\text{Shape} = \text{T shape}$	$\text{H} = sp^3d^2$ $\text{G} = \text{Octahedral}$ $\text{Shape} = \text{Square pyramid}$	$\text{Hyb} = sp^3d^3$ $\text{Geometry} = \text{Pentagonal bipyramidal}$ $\text{Shape} = \text{Pentagonal bipyramidal}$

Note: Oxoacid and peroxo acids and their ions have same hybridisation, geometry and shape.

2. Oxo-acids of halogens:

HOX , HXO_2 , HXO_3 , HXO_4 , ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ not F)

HOCl Hypochlorous acid	HClO_2 Chlorous acid	HClO_3 Chloric acid	HClO_4 Perchloric acid
ClO^- Hypochlorite ion	ClO_2^- Chlorite ion	ClO_2^- Chlorate ion	ClO_4^- Perchlorate ion
 sp^3 with 2lp $\text{SN} = 1 \text{ bp} + 3 \text{ lp} = 4$ $\text{H} = sp^3$ $\text{G} = \text{Tetrahedral}$ $\text{Shape} = \text{Linear}$	 sp^3 with 2lp $\text{SN} = 2 \text{ bp} + 2 \text{ lp} = 4$ $\text{H} = sp^3$ $\text{G} = \text{Tetrahedral}$ $\text{Shape} = \text{V or Bent}$ (one $(p\pi-d\pi)$ multiple bond)	 sp^3 with 1lp $\text{SN} = 3 \text{ bp} + 1 \text{ lp} = 4$ $\text{H} = sp^3$ $\text{G} = \text{Tetrahedral}$ $\text{Shape} = \text{Pyramidal}$ (2 $(p\pi-d\pi)$ multiple bond)	 sp^3 $\text{SN} = 4 \text{ bp}$ $\text{H} = sp^3$ $\text{G} = \text{Tetrahedral}$ (3 $(p\pi-d\pi)$ multiple bond)



Due to 4 equivalent resonance structures

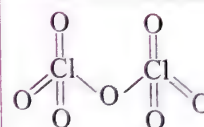
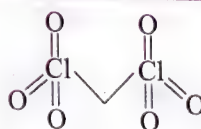
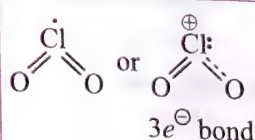
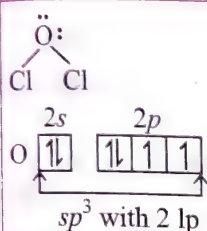
3. Oxides of chlorine:

Cl_2O
(O.S. = +1)
Chlorine monoxide

ClO_2
(O.S. = +4)
Chlorine dioxide

Cl_2O_6
(O.S. = +6)
Chlorine hexoxide
(Red, explosive liquid)

Cl_2O_7
(O.S. = +7)
Chlorine heptoxide

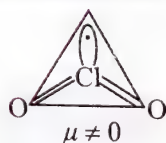
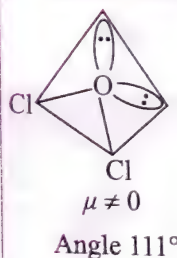


SN = 2 bp + 2 lp = 4
 $H = sp^3$
 $G = \text{T.H.}$
Shape = V or Bent

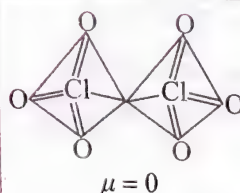
SN = 2 bp + 1 lp = 3
 $H = sp^3$
 $G = \text{Planar}$
Shape = V or bent or angular

SN = 4 bp
 $H = sp^3$
Geometry = T.H.

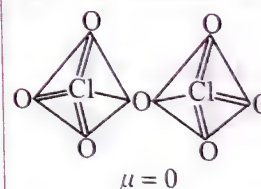
SN = 4 bp
 $H = sp^3$
Geometry = T.H.



It contains unpaired electron, so it is coloured and paramagnetic and highly reactive. It contains three electron bonds, unlike NO_2 , it does not dimerise.
[2 ($p\pi-d\pi$) multiple bond]



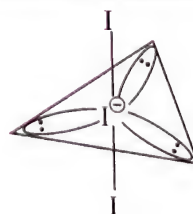
[6 ($p\pi-d\pi$) multiple bond]



[6 ($p\pi-d\pi$) multiple bond]

4. Polyhalide ion:

I_3^- (Triiodide ion)



$H = \frac{1}{2} (V + M) = \frac{1}{2} (7 + 2 + 1) = 5$ SN = 2 bp + 3lp = 5, $H = sp^3d$ $G = \text{T.b.p.}$ Shape = linear

4.1 INTRODUCTION

The five representative elements, fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) constitute group 17, and are collectively known as halogens. The name 'halogen' is derived from Greek words, 'halo' which means 'salt' and 'genes' which means 'born', i.e. salt producers. The name halogen was given to them by Schweigger in 1811 as the salts (chlorides, bromides and iodides) of first three elements occur in sea water.

Halogens are non-metallic in nature. First member of this group, i.e. fluorine is the most active and most reactive halogen and hence is also known as **super halogen**.

4.2 OCCURRENCE AND ABUNDANCE

Halogens are highly reactive elements due to high electronegativity and hence do not occur in free or native state. All halogens except astatine mainly occur in earth's crust in the combined states as halides (X^\ominus) although iodine occurs as iodate (IO_3^\ominus).

Fluorine is the thirteenth most abundant element by weight in the earth's crust, while chlorine is the twentieth. Fluorine and chlorine are reasonably abundant while bromine and iodine are comparatively rare.

Main source of **fluorine** is fluor spar or fluorite, CaF_2 . Other sources are fluoroapatite, $3Ca_3(PO_4)_2$, CaF_2 and cryolite, $Na_3[AlF_6]$. Small quantities are present in soil, river water plants and bones and teeth of animals.

The most abundant compound of **chlorine** is NaCl. Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium but is mainly NaCl solution (2.5% by

mass). The deposits of dried up seas contain sodium chloride, NaCl and carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$.

Bromine occurs in sea water and salt lakes as bromides of alkali or alkaline earth metals, e.g. KBr , $MgBr_2$ and $NaBr$.

Iodine never occurs free in nature. In combined state, it occurs as iodides and sodium iodate. Traces of compounds of this element are found in plants and animals in certain minerals and in sea water.

There are two main sources of iodine:

- Certain deep sea-weeds (Laminaria species).** These plants contain 0.5% of iodine in their ashes (known as kelp or varee) in the form of iodates.
- Caliche or crude chile saltpetre ($NaNO_3$)** which contains about 0.2% of $NaIO_3$ (sodium iodate).

The less important sources of iodine are:

- Sodium, potassium and magnesium iodide in very small amounts are found in ores of lead and dolomite.
- Sea water contains iodides and organic compounds containing iodine.
- Thyroxine which is present in thyroid gland.
- Oil-well brines contain NaI.

4.3 ATOMIC AND PHYSICAL PROPERTIES

Some of the important atomic and physical properties of group 17 elements are given in Table 4.1 and are discussed in the following sections.

Table 4.1 Atomic and physical properties of halogens

Property	Fluorine	Chlorine	Bromine	Iodine	Astatine ^{#1}
Symbol	F	Cl	Br	I	At
Atomic number	9	17	35	53	85
Atomic mass ($g\ mol^{-1}$)	19.00	35.45	79.90	126.90	210
Electronic configuration	[He] $2s^2 2p^5$	[Ne] $3s^2 3p^5$	[Ar] $3d^{10} 4s^2 4p^5$	[Kr] $4d^{10} 5s^2 5p^5$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^5$
Covalent radius (pm)	64	99	114	133	—
Ionic radius, X^\ominus (pm)	133	184	196	220	—
Ionisation enthalpy ($kJ\ mol^{-1}$)	1680	1256	1142	1008	—
Electron gain enthalpy ($kJ\ mol^{-1}$)	−333	−349	−325	−296	—
Electronegativity ^{#2}	4.0	3.2	3.0	2.7	2.2
$\Delta_{hyd} H^\ominus (X^\ominus)$ ($kJ\ mol^{-1}$)	515	381	347	305	—
	F_2	Cl_2	Br_2	I_2	—
Physical state	Gas	Gas	Liquid	Solid	—
Melting point (K)	54.4	172.0	265.8	386.6	—
Boiling point (K)	84.9	239.0	332.5	458.2	—
Density ($g\ cm^{-3}$)	1.5(85) ^{#3}	1.66 ^{#3}	3.19(273) ^{#3}	4.94(293) ^{#4}	—
Colour (gas)	Pale yellow	Yellow green	Brown red	Violet	—
Distance (X–X) (pm)	143	199	228	266	—

Bond dissociation enthalpy (kJ mol ⁻¹)	158.8	242.6	192.8	151.1	—
$E^\ominus(V^\ominus)^{\#5}$	+ 2.87	+ 1.36	+ 1.09	+ 0.54	—
$\Delta_{\text{fus}} H$ (kJ mol ⁻¹)	0.26	6.41	10.77	15.27	—
$\Delta_{\text{vap}} H$ (kJ mol ⁻¹)	3.27	20.41	31.04	43.46	—

Note: # 1: Radioactive; # 2: Pauling scale; # 3: For the liquid at temperatures (K) given in the parentheses. # 4: Solid;

5: The half cell reaction is $X_{2(g)} + 2e^\ominus \longrightarrow 2X^\ominus_{(aq)}$

4.3.1 ELECTRONIC CONFIGURATION

The general electronic configuration of group 17 elements is ns^2np^5 , i.e. all the group 17 elements have seven electrons in their valence shell, i.e., one electron short of the next noble gas.

4.3.2 ATOMIC AND IONIC RADII

Halogens have the smallest atomic radii in their respective periods. This is due to the fact that atomic radii decrease, on moving from the left to the right in the periodic table, with increase in effective nuclear charge.

Down the group (\downarrow) i.e. from F to At, atomic radii increase due to increase in number of shells, the effective nuclear charge decreases.

Atomic radii: $F < Cl < Br < I$

The ionic radii of the halide ion (X^\ominus) is always greater than the corresponding halogen (X) atom.

This is because of the fact that with the addition of an electron, effective nuclear charge decreases and the electron cloud expand.

Down the group (\downarrow), ionic radii also increase.

Ionic radii: $F^\ominus < Cl^\ominus < Br^\ominus < I^\ominus$

4.3.3 IONISATION ENTHALPY

The ionisation enthalpies of halogens are very high. Thus they have very little tendency to lose electron to form X^\oplus cation.

Down the group (\downarrow), i.e. from F to I, ionisation enthalpy decreases due to increase in the size of halogen iodine, having the lowest value of ionisation enthalpy, shows some tendency to form I^\oplus , e.g. in $[I(\text{pyridine})_2]^\oplus(\text{NO}_3)^\ominus$. I^\oplus is stabilised by forming a complex with Lewis base, pyridine.

Ionisation enthalpy: $F > Cl > Br > I$

4.3.4 ELECTRON GAIN ENTHALPY

Halogens have maximum negative electron gain enthalpy in their respective periods. This is due to the fact that halogens are just one electron short to acquire the stable electronic configuration of next noble gas. Therefore, they have strong tendency to gain an electron.

Down the group (\downarrow), electron gain enthalpies become less and less negative with the increase in the size of the halogen. However, electron gain enthalpy of F is less negative than Cl. This is due to small size of F atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of F and thus incoming electrons experience much less attraction.

Electron gain enthalpy: $Cl > F > Br > I$.

4.3.5 ELECTRONEGATIVITY

Halogens have very high value of electronegativities in their respective periods due to small size and high nuclear charge. Fluorine has been assigned the highest electronegativity of 4.0.

Down the group (\downarrow), i.e. from F to I, electronegativity decreases due to increase in size of halogen atom. Consequently, the non-metallic character decreases from F to I.

Metallic character is observed in iodine as it forms in few cases a positive ion and has a metallic lustre.

Electronegativity: $F > Cl > Br > I$

Non-metallic character: $F > Cl > Br > I$

4.3.6 ATOMICITY

All halogens exist as diatomic (X_2) molecules, with X–X bond. This is due to the fact that each halogen has one electron less than the next nearest noble gas. Hence they are highly reactive and readily share their unpaired electron with other atom to form a covalent bond.

4.3.7 PHYSICAL STATE

At room temperature, fluorine and chlorine are gases, bromine is liquid and iodine is a solid. At atmospheric pressure, I_2 solid sublimes without melting. The main reason for the change in physical state from gas (F_2 and Cl_2) to liquid (Br_2) to solid (I_2) is that down the group (\downarrow) with increase in atomic size, ease of polarisation of outer shell electrons by adjacent nuclei increases. This results in greater intermolecular attractive forces. Hence F_2 and Cl_2 exist as gases, Br_2 is a liquid and I_2 is a solid. On account of weak intermolecular forces, i.e. van der Waals forces of attraction, the halogens are volatile in native.

4.3.8 MELTING POINTS AND BOILING POINTS

Due to weak van der Waals forces of attraction between the dimeric halogen molecules, the melting points and boiling points are very low. Down the group (\downarrow), with the increase in size, ease of polarisation increases and hence melting point and boiling point increase.

Melting point: $F_2 < Cl_2 < Br_2 < I_2$

Boiling point: $F_2 < Cl_2 < Br_2 < I_2$

4.3.9 ENTHALPY OF FUSION AND VAPOURISATION

Enthalpy of fusion and vapourisation of halogens have low values due to weak van der Waals forces of attraction between halogen molecules (X_2)

Down the group (\downarrow), from F_2 to I_2 , with the increase in size, the ease of polarisation increases and hence $\Delta_{\text{fus}}H^\ominus$ and $\Delta_{\text{vap}}H^\ominus$ increases.

$$\Delta_{\text{fus}}H^\ominus: F_2 < Cl_2 < Br_2 < I_2$$

$$\Delta_{\text{vap}}H^\ominus: F_2 < Cl_2 < Br_2 < I_2$$

4.3.10 NON-METALLIC CHARACTER

Halogens are non-metallic in nature, due to their very high values of ionisation enthalpy and electronegativity. Down the group, non-metallic character decreases due to decrease in the value of ionisation enthalpy and electronegativity. In fact, iodine is a solid and possesses metallic lustre.

4.3.11 BOND DISSOCIATION ENTHALPY

Halogens exist as diatomic molecules. It would be expected that bond dissociation enthalpy, i.e. the energy required to dissociate the halogen molecule (X_2) into halogen atom (X) would decrease down the group (\downarrow). This is due to the fact that with the increase in atomic size, the effective overlap of orbitals resulting in $X-X$ bond formation decreases. Cl_2 , Br_2 and I_2 show the expected trend, **but the bond dissociation enthalpy of F_2 is less than Br_2 and Cl_2 .**

$$Cl_2 > Br_2 > F_2 > I_2$$

Abnormally low bond dissociation enthalpy of F_2 is largely responsible for its high reactivity. Two different explanations have been suggested for low bond dissociation enthalpy of F_2 :

The large electron-electron repulsions between the lone pairs of electrons on the two fluorine atoms weaken the bond.

4.3.12 COLOUR

All the halogen molecules are coloured and the colour changes with increasing size of the halogen molecule.

Halogen	F_2	Cl_2	Br_2	I_2
Colour	Pale yellow	Yellow green	Reddish brown	Violet

The colour is due to absorption of light in the visible region. The energy acquired in this manner excites the valence electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), i.e. transition from π^* to σ^* molecular orbital.

On de-excitation, the energy of transmitted light falls in visible region and the colour of halogen is actually the colour of this transmitted light, i.e. halogens have complementary colour.

The excitation energy, i.e. the amount of energy required for the excitation decreases progressively from F_2 to I_2 , with the increase in atomic size. Conversely, energy of transmitted light increases progressively. Hence there is progressive deepening of colours down the group, i.e. from F_2 to I_2 .

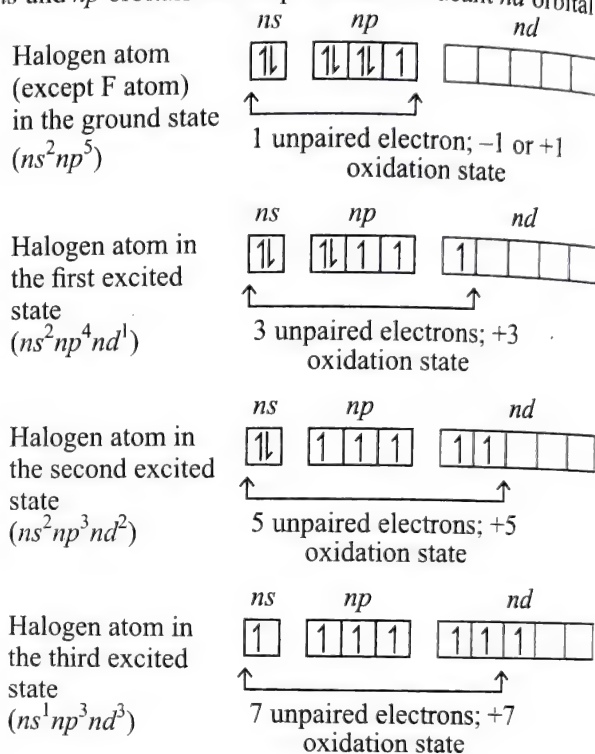
The F_2 molecule is small, in which the valence electrons are held tightly. Thus it absorbs high energy violet radiation and appears pale yellow.

The larger I_2 molecule absorbs low-energy yellow and green radiations and appears violet. Change in colour on moving down the group is known as bathochromic shift.

4.4 CHEMICAL PROPERTIES

4.4.1 NATURE OF BONDS AND OXIDATION STATES

When the halogen atom combines with an element of lesser electronegativity, it shows -1 oxidation state, on the other hand, when it combines with an element of higher electronegativity, it exhibits $+1$ oxidation state. Fluorine, having the highest electronegativity, shows -1 oxidation state, except in $HO\ddot{O}F$, where the oxidation state of F is $+1$. The other halogens i.e. Cl , Br and I , in addition to an oxidation state of -1 , also shows positive oxidation $+1$ and highest oxidation states of $+3$, $+5$ and $+7$ as the electrons in ns and np orbitals can be promoted to vacant nd orbital.



F atom has no d -orbitals in the valency shell, thus, it cannot have any excited state and cannot show any of the higher oxidation states.

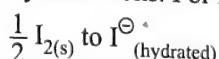
In addition to the above-mentioned positive oxidation states, Cl , Br and I also show an oxidation state of $+4$ (in ClO_2) and $+6$ (in Cl_2O_6 and ClO_3) while Br shows an oxidation state of $+4$ (in BrO_2).

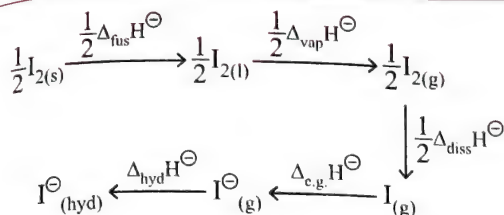
4.4.2 OXIDISING POWER

Electron affinity is the tendency of the atoms to gain electrons. Chlorine has the highest electron affinity. Oxidation may be regarded as the removal of electrons, so that an oxidising agent gains electrons. Thus the halogens, which have strong tendency to accept an electron, act as strong oxidising agents, and their oxidising power decreases from fluorine to iodine.

	F_2	Cl_2	Br_2	I_2
$E^\ominus(V)$	+2.87	+1.36	+1.09	+0.54

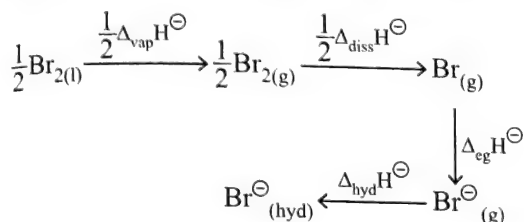
The strength of oxidising agent (that is oxidation potential) depends on several energy terms. The oxidation potential is the energy change between the element in its standard state and in its hydrated ions. For iodine, the change is from





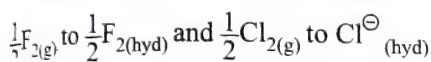
$$E = \frac{1}{2} \Delta_{\text{fus}} \text{H}^\ominus + \frac{1}{2} \Delta_{\text{vap}} \text{H}^\ominus + \frac{1}{2} \Delta_{\text{diss}} \text{H}^\ominus + \Delta_{\text{e.g.}} \text{H}^\ominus + \Delta_{\text{hyd}} \text{H}^\ominus$$

For bromine, the change is from $\frac{1}{2} \text{Br}_{2(l)}$ to $\text{Br}^\ominus_{(\text{hyd})}$.



$$E = \frac{1}{2} \Delta_{\text{vap}} \text{H}^\ominus + \frac{1}{2} \Delta_{\text{diss}} \text{H}^\ominus + \frac{1}{2} \Delta_{\text{e.g.}} \text{H}^\ominus + \Delta_{\text{hyd}} \text{H}^\ominus$$

For fluorine and chlorine, the change is from



$$E = \frac{1}{2} \Delta_{\text{diss}} \text{H}^\ominus + \Delta_{\text{e.g.}} \text{H}^\ominus + \Delta_{\text{hyd}} \text{H}^\ominus$$

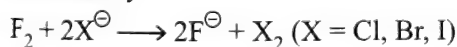
Chlorine has highest electron gain enthalpy, so gaseous Cl can accept electron most readily. However, chlorine is not the strongest oxidising agent. Fluorine acts as the strongest oxidising agent and the oxidising power decreases from F_2 to I_2 .

Oxidising power: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

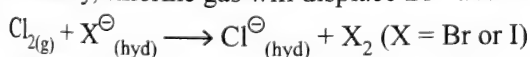
This is due to:

- F_2 has a low enthalpy of dissociation due to weakness of F-F bond.
- F_2 has a high free energy of hydration due to smallest size of F^\ominus ion.

Fluorine will oxidise other halide ions to halogens in solution or when dry.



Similarly, chlorine gas will displace Br^\ominus and I^\ominus from solution.

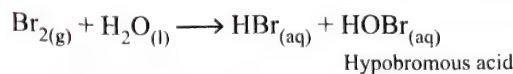
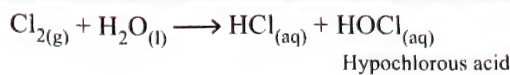
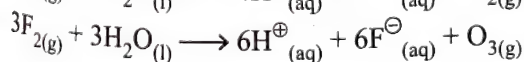
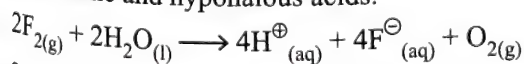


This is the basis of commercial extraction of bromine from sea water.

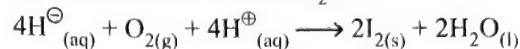
In general, any halogen of lower atomic number will oxidise the halide ion of higher atomic number.

Thus, a stronger oxidising halogen can be used to prepare a weaker oxidising halogen from its anion. For example, Cl_2 water is used to produce Br_2 and I_2 from Br^\ominus and I^\ominus solutions respectively.

The relative oxidising power of halogens can further be illustrated by their reactions with water. F_2 oxidises H_2O to O_2 and O_3 whereas Cl_2 and Br_2 react with water to form corresponding hydrohalic and hypohalous acids.



The reaction of I_2 and H_2O is non-spontaneous. In fact, I^\ominus ions can be oxidised by O_2 in acidic medium which is just the reverse of reaction observed with F_2 .



The halide ions act as reducing agents. I^\ominus ion does not show any reducing nature but Cl^\ominus , Br^\ominus and I^\ominus ions act as reducing agents and their reducing nature is in increasing order.

Reducing nature: $\text{F}^\ominus < \text{Cl}^\ominus < \text{Br}^\ominus < \text{I}^\ominus$

ILLUSTRATION 4.1

Explain:

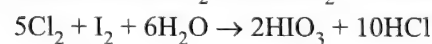
- Addition of Cl_2 to KI solution gives it a violet colour but excess of Cl_2 turns it colourless.
- Slow Cl_2 can be prepared from HCl and HCl from Cl_2 ?
- F_2 is a non-metal whereas I_2 shows some metallic properties.
- Metal fluorides are more ionic than metal chlorides.

Sol.

- Since I^\ominus is a stronger oxidising agent thus Cl_2 releases I_2 and gives violet colour.

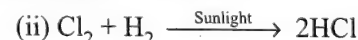


But excess of Cl_2 oxidises I_2 to colourless Iodic acid



(colourless)

- (i) $\text{MnO}_2 + 4\text{HCl} \longrightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$



- Due to high I.E. and small size of F, it has no tendency to lose e^- . Whereas, due of low I.E. and large size of I, it can lose e^- 's and shows electropositive nature i.e., metallic nature.
- According to Fajan's rule:
 - Small cation, large anion more covalent character.
 - Large cation, small anion \propto more ionic character.

Size of $\text{Cl}^\ominus >$ Size of F^\ominus

Thus metal fluorides are more ionic than metal chlorides.

4.5 CHEMICAL CHARACTERISTICS

Halogens are highly reactive non-metallic due to:

- Low bond dissociation enthalpy ($\text{X}_2 \longrightarrow 2\text{X}$):** Halogens have low bond dissociation enthalpy as compared to common molecules like H_2 , O_2 , N_2 , etc. Therefore, they readily dissociate into atoms and react with other substances readily.
- High negative electron gain enthalpies:** Due to high negative electron gain enthalpies, halogens have a very strong tendency to gain an electron and thus are very reactive,

They react with metals and non-metals to form halides. However, down the group (\downarrow), the reactivity decreases in the order: $F_2 > Cl_2 > Br_2 > I_2$.

4.5.1 REACTIVITY TOWARDS HYDROGEN

All the halogens react with hydrogen to form volatile, covalent hydrides of formula HX . These hydrides are called hydracids or halogen acids. The activity of halogens towards hydrogen decreases from fluorine to iodine.

Hydrogen combines explosively with fluorine even in dark. It combines with chlorine in presence of sunlight and with bromine on heating. Hydrogen combines with iodine on heating and in presence of a catalyst. The reaction with iodine is reversible and incomplete.

4.5.2 REACTIVITY TOWARDS OXYGEN

Halogens form many binary compounds with oxygen but most of them are unstable.

Compounds of fluorine and oxygen are referred to as fluorides of oxygen and not oxides of fluorine as fluorine is more electronegative than oxygen. The compounds of Cl , Br and I with oxygen are termed as oxides.

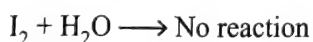
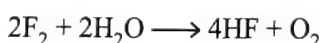
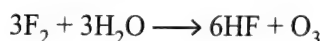
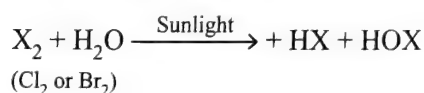
Chlorine, bromine and iodine form oxides in which the oxidation states of halogens range from +1 to +7. Chlorine forms the largest number of oxides while iodine forms the least. In these binary compounds, the bonds are mainly covalent due to small difference in electronegativity between the halogens and oxygen; the bond polarity, however, increases from Cl to I . The stability of oxides of iodine is greater than those of chlorine while bromine oxides are the least stable. Iodine—oxygen bond is stable due to greater polarity of the bond while the stability of the chlorine—oxygen bond is due to multiple bond formation involving d -orbitals of the chlorine atom. Bromine being in between lacks both these characteristics. Thus, the stability of oxides of halogens decreases in the order: $I > Cl > Br$. Further the higher oxides of halogens tend to be more stable than the lower ones.

4.5.3 REACTIVITY TOWARDS HALOGENS

Halogens react with each other to form a number of compounds known as interhalogen compounds.

4.5.4 REACTIVITY TOWARDS WATER

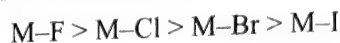
Fluorine decomposes water very readily even at low temperature and in dark forming mixture of O_2 and O_3 , Cl_2 decomposes water in presence of sunlight while bromine decomposes water very slowly in presence of sunlight. Iodine does not decompose water.



4.5.5 REACTIVITY TOWARDS METALS AND NON-METALS

Due to high oxidising power, halogens combine directly with most metals to form their corresponding halides. Nearly all metals combine with F_2 either in cold or on heating to form fluorides. Chlorine combines with large number of metals but slowly. Bromine and iodine do not react with non-metals, like Au , Pt and even with less active metals.

As expected, the ionic character of the $M-X$ bond, decreases in the order:



This is due to a corresponding decrease in the electro-negativity of the halogen from F to I . However, if the metal exhibits more than one oxidation states, the halide in the higher oxidation state will be more covalent than the one in the lower oxidation state. For example, $SnCl_4$, $PbCl_4$, $SbCl_5$, UF_6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4 respectively.

Halogens also combine with a number of non-metals like S , P , As , etc. The reactivity decreases from fluorine to chlorine. For example, sulphur forms hexafluoride with fluorine (SF_6), tetrachloride with chlorine (SCl_4) and dibromide with bromine (SBr_2) and there is no reaction between sulphur and iodine.

4.6 ANOMALOUS BEHAVIOUR OF FLUORINE

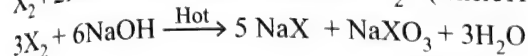
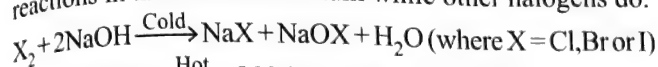
Fluorine, the first member of group 17 elements, differs from other members of its group, due to the following reasons:

- Smallest size of the atom
- Highest electronegativity
- Absence of d -orbitals in its valence shell
- Low bond-dissociation enthalpy of F_2 molecule.

The main points of difference are as follows:

1. **Reactivity:** Fluorine is the most reactive as bond dissociation energy of $F-F$ bond is low. $X-X$ bond is the stronger in Cl_2 and Br_2 .
2. Maximum covalency of fluorine is one as there is no d -orbital in its valence shell. Other members can have maximum covalency of 7 because of vacant d -orbitals.
3. HF is a weak acid in comparison to HCl , HBr and HI under similar circumstances. HF is a liquid (b.pt. $19^\circ C$) while HCl , HBr and HI are gases under ordinary conditions. This is due to presence of hydrogen bonding in HF while hydrogen bonding is not present in HCl , HBr and HI .
4. **Oxidation state:** Since it is the most electronegative element it shows an oxidation state of -1 , except $+1$ in HOX . Further, it does not show any higher oxidation states (positive or negative) because of the absence of d -orbitals in its valence shell. Other members, however, show both negative oxidation state of -1 and different positive oxidation states of $+1$, $+3$, $+5$ and $+7$.

Since fluorine usually does not show positive oxidation states, therefore, F_2 does not undergo disproportionation reactions in the alkaline medium while other halogens do.



(where $X = Cl, Br \text{ or } I$)

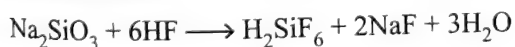
5. **Hydrogen bonding:** Hydrogen bonding is a distinct phenomenon observed in some fluorine compounds due to small atomic size and high electronegativity of fluorine.

- HF is a liquid with a boiling point of 293 K while other halogen halides are gases under ordinary conditions with low boiling points.
- HF is a weak acid as compared to other halogen acids which are strong and highly ionised. This is due to higher dissociation energy of H-F bond and molecular association due to hydrogen bonding in HF.
- Due to hydrogen bonding, HF can form acid salts of the type KHF_2 , i.e., $[K^+ (F-H-F)^-]$ while other halogen acids do not form such compounds.

6. **Nature of compounds:** Due to its highest electronegativity, fluorine has the highest tendency to form ionic compounds and thus fluorides have the maximum ionic character. For example, AlF_3 is ionic whereas other halides of aluminium are covalent.

7. **Oxidising power:** Fluorine has the highest electrode potential. Thus, it is reduced most easily and hence acts as the strongest oxidising agent among the halogens. It brings about highest oxidation state of other elements with which it combines. For example, with sulphur it gives SF_6 and with osmium it gives OsF_8 . Other halogens do not always bring about the highest oxidation state of the element. It can oxidise most of the other elements, including some of the noble gases (Kr and Xe).

8. **Reactivity of halogen acids:** HF although weak, is the most reactive of all halogen acids. It can attack glass because of its ability to displace oxygen from silicates to form fluorosilicates.



That is why HF is used for etching of glass, in marking thermometers, burettes, etc. Other halogen acids, i.e., HCl, HBr and HI do not give this reaction.

Due to the above special properties of fluorine, it is usually called as super halogen.

- AgF is soluble in water while AgCl, AgBr and AgI are insoluble in water. Similarly, calcium fluoride is insoluble and other halides of calcium are soluble.
- Fluorine combines with sulphur to form SF_6 but no other halogen forms the hexahalide with sulphur.
- Fluorine does not form any oxyacid but other halogens form a number of oxyacids.
- It directly combines with carbon while other halogens do not react even under drastic conditions.

13. Ozone is formed when fluorine decomposes water. Ozone is not formed when other halogens react with water.

14. Fluorine does not form any oxysalt when it reacts with alkalies while other halogens form oxysalts with alkalies.

15. Fluorides are more stable than corresponding chlorine compounds. For example, UF_6 is more stable than UCl_6 , NF_3 is non-explosive while NCl_3 is highly explosive.

16. The fluoride ion has a great tendency to form complex ions, e.g., $[AlF_6]^{3-}$, $[FeF_6]^{3-}$. The remaining halide ions show this tendency to a much lesser extent.

17. Fluorine does not have a vacant d -orbital in valence shell, therefore it does not combine with F ion to form polyfluoride ions like Cl_3^- , Br_3^- , I_3^- , I_5^- , etc.

ILLUSTRATION 4.2

- Halogens have maximum negative gain enthalpy in the respective periods of the periodic table. Why?
- Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?
- Fluorine exhibits only -1 oxidation state, whereas other halogens exhibit $+1$, $+3$, $+5$ and $+7$ oxidation states also. Explain.

Sol.

- Halogens have the smallest size in their respective periods and therefore high effective nuclear charge. As a consequence, they readily accept one electron to acquire noble gas configuration.
- Fluorine is a stronger oxidising agent than chlorine, due to:
 - Low enthalpy of dissociation of F-F bond
 - High hydration enthalpy of fluorine.
- Fluorine is the most electronegative element and cannot exhibit positive oxidation state. Other halogens have vacant d -orbitals and therefore, can expand their octets and show $+1$, $+3$, $+5$ and $+7$ oxidation states also.

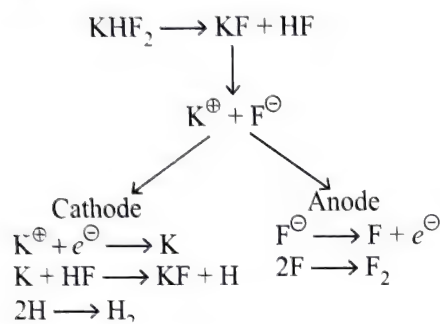
4.7 FLUORINE

Fluorine presented many difficulties in its isolation and was isolated by **Moissan** in 1886. **The reasons for its late discovery were its high reactivity and non-conducting nature of hydrofluoric acid.** Fluorine attacked the material of the vessels used for its isolation. Carbon vessel was attacked with formation of CF_4 and platinum vessel was reduced to chocolate powder. The vessels of other metals were also affected. The platinum and carbon could not be used as electrodes. Another difficulty experienced was that when the electrolysis of aqueous HF acid was carried out, hydrogen and ozone were obtained and when anhydrous hydrofluoric acid was tried it was found to be a bad conductor of electricity.

Moissan finally isolated fluorine by the electrolysis of anhydrous hydrofluoric acid in the presence of potassium hydrogen fluoride using Pt–Ir alloy vessel at -23°C . The electrodes used were also of Pt–Ir alloy.

Modern methods of isolation: In modern methods, fluorine is prepared by electrolysis of a fused fluoride (usually potassium hydrogen fluoride, KHF_2). The electrolytic cells are made of copper, nickel or monel metal. The anode is generally of graphite and the fluorine set free contains some carbon tetrafluoride.

Reactions in the electrolytic cell



Following precautions should be taken in the preparation of fluorine:

- The electrolyte must be completely dry. In presence of moisture, the evolved fluorine reacts with moisture to form O_2 and O_3 .
- The parts of the apparatus which come in contact with fluorine must be free from oil and grease.
- The vessel in which fluorine is collected should also be absolutely dry.
- The gas must be made free from HF before storing by passing through sodium fluoride (NaF) otherwise HF will attack vessel. HF is more corrosive and reactive than fluorine.

Properties:

(A) Physical properties

- The gas is pale greenish yellow in colour. It can be condensed to yellow liquid at -188°C and pale yellow solid at -223°C .
- It has pungent odour resembling that of a mixture of ozone and chlorine. It is a poisonous gas but less poisonous than HF gas. It is the most reactive element.

(B) Chemical properties

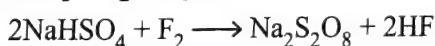
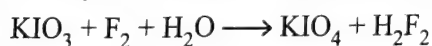
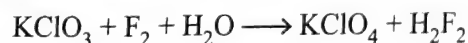
- Fluorine reacts vigorously with water to give O_2 and O_3 .

$$2\text{H}_2\text{O} + 2\text{F}_2 \longrightarrow 4\text{HF} + \text{O}_2$$

$$3\text{H}_2\text{O} + 3\text{F}_2 \longrightarrow 6\text{HF} + \text{O}_3$$
- Fluorine reacts with dilute alkalies to form oxygen difluoride (OF_2) and with conc. alkalies O_2 is formed.

$$2\text{F}_2 + 2\text{NaOH} \longrightarrow \text{OF}_2 + 2\text{NaF} + \text{H}_2\text{O}$$

$$2\text{F}_2 + 4\text{NaOH} \longrightarrow 4\text{NaF} + 2\text{H}_2\text{O} + \text{O}_2$$
- It acts as a strong oxidising agent. It oxidises chlorates to perchlorates, iodates to periodates and bisulphates to peroxysulphates.



- It attacks glass at about 100°C forming SiF_4 . However, the attack of dry fluorine is slow. At low temperatures, dry fluorine can be stored in dry glass vessel.

Uses:

- It is used as an insecticide.
- It is extensively used for the preparation of various fluorine compounds which have wide applications.
 - Freon, CCl_2F_2 (dichloro difluoro methane), is used in refrigerators and cold storage plants.
 - Teflon (C_2F_4), a new plastic, has a very high electrical resistance and is used as insulating material in cables. Teflon is not affected by acids, alkalies and strong oxidising agents.
 - H_2F_2 is used for etching of glass and for removing silica from iron castings.

$$\text{SiO}_2 + 2\text{H}_2\text{F}_2 \longrightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$$
 - UF_6 is used in the separation of ^{235}U from natural uranium by diffusion method.
 - SF_6 has insulating properties. It is used in X-ray and high voltage machines.
 - Sodium fluoroacetate is used as a rat poison.
 - NaF and Na_3AlF_6 (cryolite) are used as insecticides.
 - CuF_2 is used in the ceramic industry and as a flux in soldering, welding and glazing.

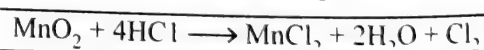
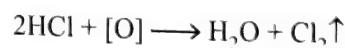
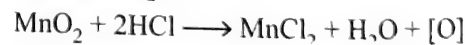
4.8 CHLORINE

Chlorine was discovered by **Scheele** in 1774 by the action of HCl on MnO_2 . **Berthollet** named this gas oxy muriatic acid gas since he thought it to be an oxide of muriatic acid (old name of HCl). In 1810, **Davy** established its elementary nature and named it chlorine on account of its greenish yellow colour (**Greek word, 'chloros' which means 'greenish yellow'**).

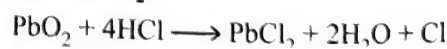
Preparation:

- By the oxidation of hydrochloric acid:** The oxidising agents which can be used are MnO_2 , PbO_2 , Pb_3O_4 (red lead), KMnO_4 (potassium permanganate), $\text{K}_2\text{Cr}_2\text{O}_7$ (potassium dichromate), NaOCl (sodium hypochlorite), O_3 , etc. In all these reactions, HCl acts as a reducing agent.

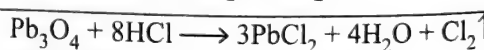
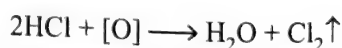
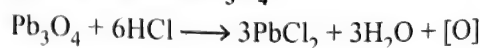
i. With MnO_2 :

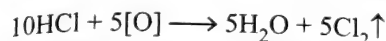
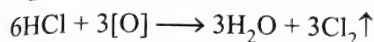
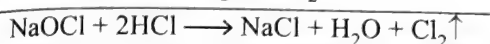
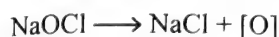
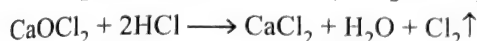
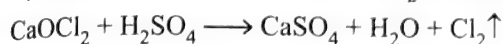
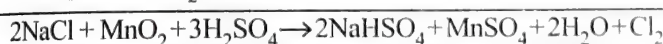
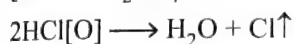
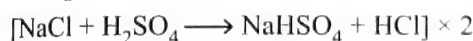
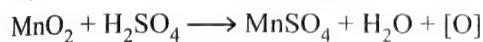
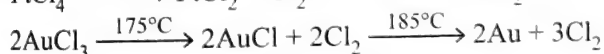
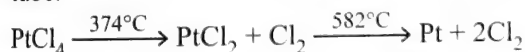
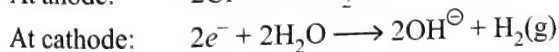
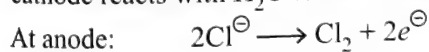


ii. With PbO_2 :



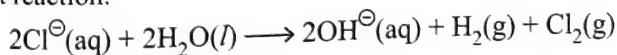
iii. With red lead, Pb_3O_4 :



iv. **With KMnO_4 :**v. **With $\text{K}_2\text{Cr}_2\text{O}_7$:**vi. **With NaOCl :**vii. $\text{O}_3 + 2\text{HCl} \longrightarrow \text{O}_2 + \text{H}_2\text{O} + \text{Cl}_2 \uparrow$ 2. By the action of mineral acids or CO_2 on bleaching powder.3. In laboratory, Cl_2 is prepared by heating with concentrated H_2SO_4 in presence of MnO_2 .4. Pure chlorine may be obtained by heating dry platinum chloride (PtCl_4) or gold chloride (AuCl_3) in a hard glass tube.**Manufacture of chlorine:**1. **Electrolytic process:** Chlorine is obtained by the electrolysis of a concentrated solution of NaCl (brine), when Cl_2 is liberated at the anode and the sodium metal liberated at the cathode reacts with H_2O to form NaOH and H_2 .

(Since the reduction potential of H_2O > reduction potential of Na , so reduction of H_2O occurs)

Net reaction:



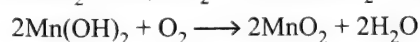
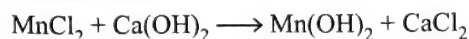
For the given reaction, $\Delta_r G^\ominus$ is +422 J.

Therefore, an external e.m.f. more than 2.2 V is required for the extraction of Cl_2 from brine.

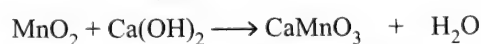
It is also obtained as a by product during manufacture of sodium by electrolysis of fused NaCl in **Down's process**.

2. **Weldon's process:** It involves the heating of pyrolusite mineral (MnO_2) with concentrated hydrochloric acid in stone-ware stills.

The manganese chloride present in the waste liquor is converted into a product which can be used instead of fresh pyrolusite for oxidising more of hydrochloric acid. The manganese chloride solution is mixed with excess of lime and air is blown in the heated mixture. The following changes occur:

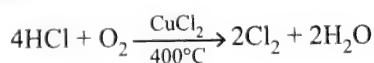


(Air)

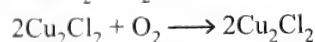
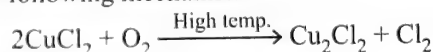


Calcium manganite

Calcium manganite settles down to the bottom as a dark coloured mud. This is used for oxidation of fresh quantities of hydrochloric acid.

3. **Deacon's process:** Deacon's process is superior to Weldon's process. In this process, chlorine is obtained by the oxidation of HCl with air in presence of cupric chloride heated to 400°C .

The catalytic action of cupric chloride can be explained with the following mechanism.

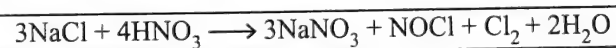
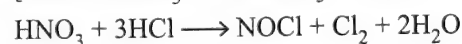
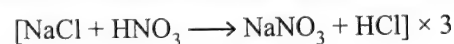


Air

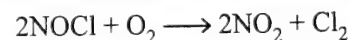
Copper oxychloride



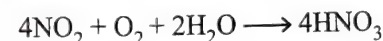
The cycle is then repeated, the gaseous products being steam and chlorine.

4. **Nitrosyl chloride process:** In this process, common salt (NaCl) is treated with concentrated nitric acid, when a mixture of chlorine and nitrosyl chloride is evolved.

The gaseous mixture is oxidised with oxygen.



The gases are liquefied and chlorine distilled out. Nitrogen dioxide is absorbed in water in presence of oxygen to form nitric acid which can be used again.



Nowadays, due to economical reasons, nitrosyl chloride process is used to manufacture chlorine.

Storage and transportation of chlorine: Chlorine is stored and transported in the liquid state. The liquid is stored in large steel tanks which are kept in heat-insulated cold storage rooms.

Properties:**(A) Physical properties**

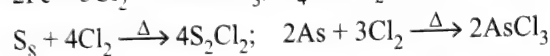
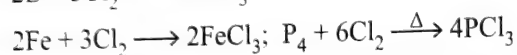
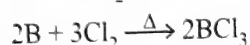
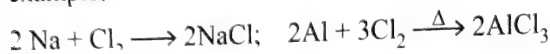
1. It is a greenish yellow gas with pungent and suffocating odour.

- It is 2.5 times heavier than air.
- It can be easily liquefied into greenish yellow liquid which boils at 239 K.
- It is fairly soluble in water. The aqueous solution is called **chlorine water**. It has yellow colour and smells of chlorine. At 0°C, crystals of chlorine hydrate, $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ are formed.

(B) Chemical properties

1. **Combustibility:** Chlorine does not burn and also does not help in burning.

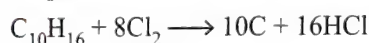
2. **Reaction with metals, non-metals and metalloids:** Chlorine reacts with a number of metals, non-metals and metalloids to form their corresponding chlorides. For example,



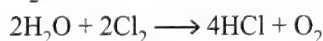
It combines with all the non-metals, except N_2 , O_2 , C and inert gases. It combines with H_2 in light (but not in dark) with explosion to form HCl. However, in presence of charcoal as a catalyst, the reaction is safe.

3. **Affinity for hydrogen:** It has great affinity for hydrogen. It decomposes several hydrogen compounds forming HCl.

i. Turpentine burns in chlorine forming HCl and carbon.

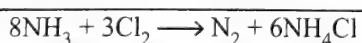
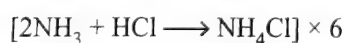
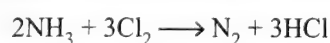


ii. It reacts with water in the presence of sunlight and forms O_2 .

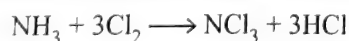


iii. It reacts with ammonia under two conditions:

a. **When ammonia is in excess:** The products are nitrogen and ammonium chloride.



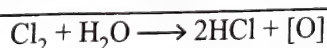
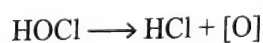
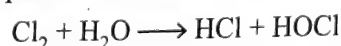
b. **When chlorine is in excess:** The products are nitrogen trichloride (explosive) and HCl.



iv. It removes hydrogen from H_2S .

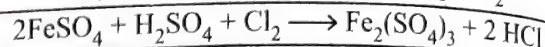
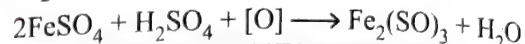
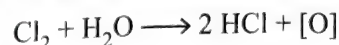


4. **Oxidising properties:** In presence of moisture, Cl_2 acts as an oxidising agent. When Cl_2 is dissolved in water it forms chlorine water. On standing, chlorine water loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) thus formed, being unstable, decomposes to give nascent oxygen which is responsible for oxidising properties of chlorine.

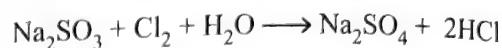


Thus, in presence of moisture or in aqueous solution, Cl_2 acts as a strong oxidising agent.

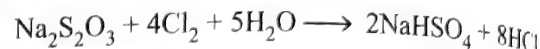
a. Oxidises acidified ferrous to ferric salts.



b. Oxidises sulphites to sulphates.

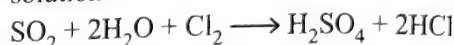


c. Oxidises thiosulphates to bisulphates

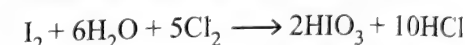


Sodium thiosulphate

d. Oxidises sulphur dioxide to sulphuric acid in aqueous solution



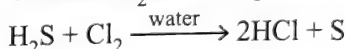
e. Oxidises moist iodine to iodic acid.



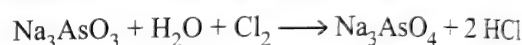
Iodine

Iodic acid

f. Oxidises H_2S to S in presence of water.



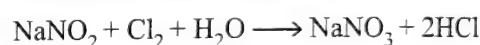
g. Oxidises sodium arsenite to sodium arsenate.



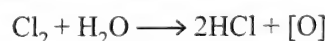
Sodium arsenite

Sodium arsenate

h. Oxidises nitrites to nitrates



5. **Bleaching action:** In presence of moisture or in aqueous solution, Cl_2 acts as a powerful bleaching agent and bleaches vegetable or organic matter.



Coloured substance + $[\text{O}] \longrightarrow$ Colourless substance

The bleaching action of Cl_2 is due to oxidation of coloured substances to colourless substances by nascent oxygen.

Since the bleaching action of Cl_2 is due to oxidation while that of SO_2 is due to reduction, hence, bleaching effect of Cl_2 is permanent while that of SO_2 temporary.

6. **Reaction with cold and hot alkalis:** When Cl_2 is passed into cold dilute solution of alkalis, a mixture of chloride and hypochlorite is formed.

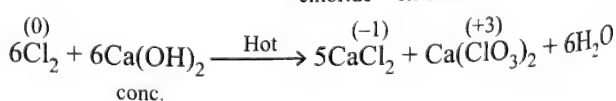
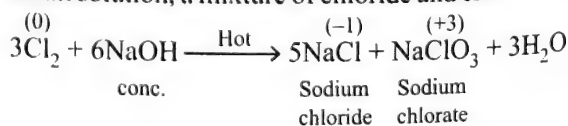


Sodium chloride Sodium hypochlorite



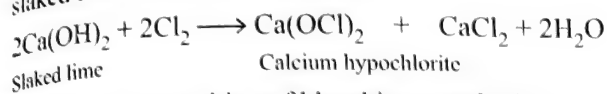
Calcium chloride Calcium hypochlorite

However, when Cl_2 is passed through hot and concentrated alkali solution, a mixture of chloride and chlorate is formed.

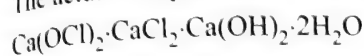


During these reactions, chlorine is simultaneously reduced to chloride ion, Cl^- and oxidised to either hypochlorite (^-OCl) or chlorate (ClO_3^-) ion. Such reaction which involves simultaneous oxidation-reduction is known as disproportionation reaction.

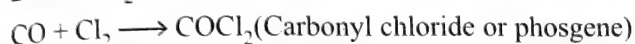
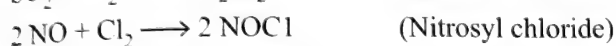
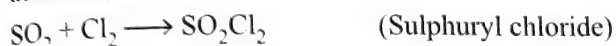
7. **Reaction with dry slaked lime:** Chlorine reacts with dry slaked lime to form bleaching powder.



The actual composition of bleaching powder is



- b. Cl_2 also reacts with many non-metal oxides to form addition products.



Uses:

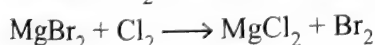
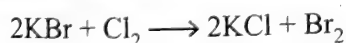
- i. For bleaching wood pulp (required for manufacture of paper and rayon), cotton and textiles.
- ii. In the manufacture of dyes, drugs and organic compounds such as CHCl_3 , CCl_4 , DDT, refrigerants (CCl_2F_2 , freon) and bleaching powder.
- iii. In the metallurgy (extraction) of gold and platinum.
- iv. In sterilising drinking water.
- v. In the preparation of poisonous gases like phosgene (COCl_2), tear gas ($\text{CCl}_3 \cdot \text{NO}_2$), mustard gas ($\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$), etc. Mustard gas was used by Germany in World War I.
- vi. As a germicide and disinfectant.

4.9 BROMINE

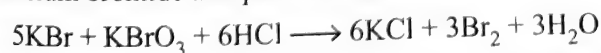
Bromine was discovered in 1826 by the French chemist **Balard** in the mother liquor left after the crystallisation of common salt from sea water. The name bromine was given due to its bad and pungent odour (**Greek word, 'Bromos', which means 'stench'**).

Preparation:

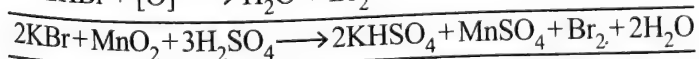
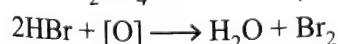
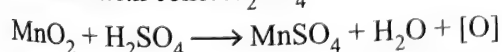
1. By passing chlorine through the solution of potassium or magnesium bromide.



2. By adding hydrochloric acid to the mixture containing potassium bromide and potassium bromate.



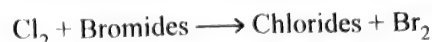
3. By heating mixture of potassium bromide and manganese dioxide with conc. H_2SO_4 .



This reaction is commonly used in the laboratory for the preparation of bromine (Br_2).

Manufacture:

1. **From sea water:** Sea water is the most important source of commercial bromine. The sea water is slightly acidified and then treated with chlorine to liberate the bromine.

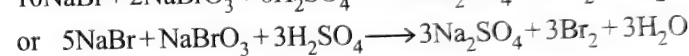
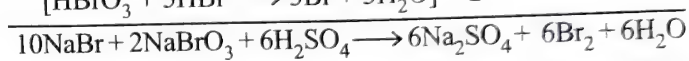
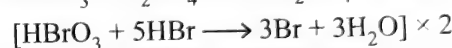
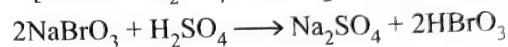
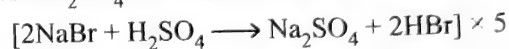


(Sea water)

The evolved bromine is blown out by means of a current of air. The air carrying the bromine vapours is passed through absorption towers down which a sodium carbonate solution is sprayed. The bromide combines forming sodium bromate and sodium bromide.



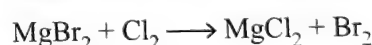
The solution containing bromide and bromate is distilled with H_2SO_4 to recover bromine.



The vapours are condensed.

2. **From carnallite mother liquor:** The mother liquor left after the crystallisation of potassium chloride from carnallite contains about 0.25% of bromine as magnesium bromide and potassium bromide and is known as *bittern*.

The hot mother liquor is made to flow down a tower packed with earthen-ware balls. A current of chlorine and steam is introduced from the bottom of the tower. The vapours of bromine set free are condensed in a condenser.



Properties:

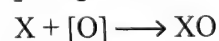
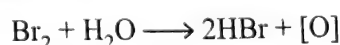
(A) Physical properties

1. It is a reddish brown, heavy mobile liquid.
2. Its density is 3.2.
3. It has irritating bad odour.
4. It freezes to give yellowish brown solid.
5. Br_2 vapours attack the eyes and mucous membrane of nose and throat. It brings blisters on the skin which take a very long time to heal. It is highly poisonous.
6. It is fairly soluble in water (3.6% at 20°C). The solution is termed bromine water. A saturated solution of bromine when cooled in a freezing mixture gives $\text{Br}_2 \cdot 8\text{H}_2\text{O}$.
7. It is more soluble in chloroform, carbon tetrachloride, etc.

The colour of the solution is usually reddish brown.

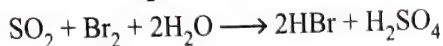
(B) Chemical properties: Br_2 closely resembles Cl_2 in its properties.

1. **Oxidising properties:** Bromine is a good oxidising agent. It ordinarily does not react with water but in presence of an oxidisable substance forms hydrogen bromide and oxygen with water.

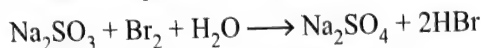


Oxidisable substance

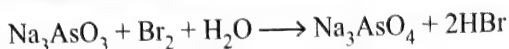
a. Oxidises SO_2 to sulphuric acid.



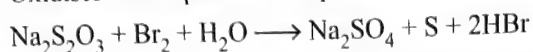
b. Oxidises sulphites to sulphates.



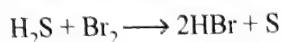
c. Oxidises arsenites to arsenates.



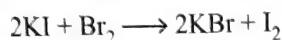
d. Oxidises thiosulphates to sulphate.



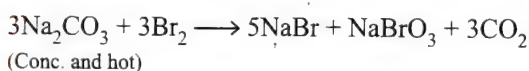
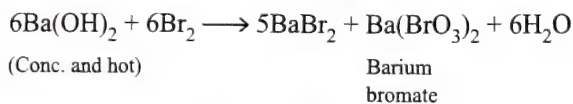
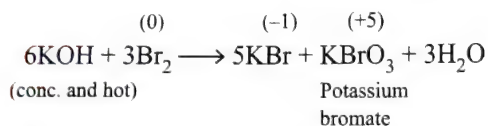
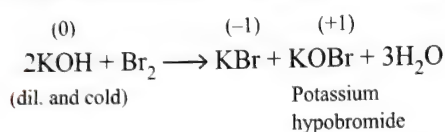
e. Sulphur is formed by oxidation of hydrogen sulphide.



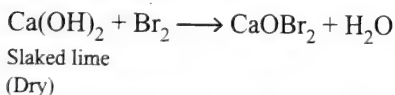
f. Iodine is liberated from iodides.



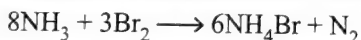
2. **Reactions with alkalis:** The action of bromine on alkalis is similar to that of chlorine, a hypobromite with a cold dilute solution and a bromate with a hot solution are formed.



However, with slaked lime (dry) it forms a compound similar to bleaching powder.



3. **Reaction with ammonia:** It is similar to that of chlorine.



4. **Bleaching action:** The bleaching action of bromine is weaker than that of chlorine. The bleaching action is due to its oxidising property.

Uses:

- The chief use of bromine is in the manufacture of ethylene bromide ($\text{C}_2\text{H}_4\text{Br}_2$) which is extensively employed as a component of anti-knock gasoline.
- In the manufacture of NaBr and KBr (used in medicine as sedative), and certain organic dyes.
- Bromine water is used in organic chemistry to test the unsaturation of organic compounds.
- As germicide.
- It is used as an oxidising agent and in organic synthesis.

4.10 IODINE

Iodine was discovered by **Bernard Courtois** in 1812 from the ashes of sea-weeds. Gay-Lussac established its elementary nature

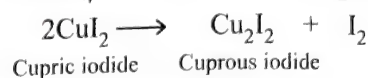
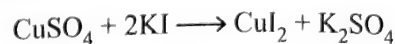
and named it iodine on account of the violet colour of its vapours (Greek word, 'Iodos' which means 'violet').

Properties:

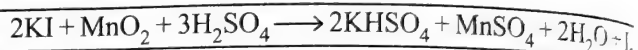
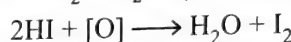
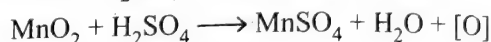
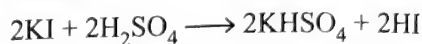
1. By passing chlorine through potassium iodide solution.



2. By adding potassium iodide solution to copper sulphate solution.



3. By heating mixture of potassium iodide and manganese dioxide with conc. H_2SO_4 .

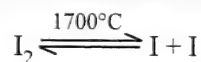


In laboratory, iodine is usually prepared by this reaction.

Properties:

(A) Physical properties

- It is a black (dark violet) shining solid, i.e., it has metallic lustre.
- It sublimes rapidly below melting point giving violet coloured vapours.
- Iodine produces stains on skin, its vapours are pungent and irritating and very dangerous to inhale.
- Its specific gravity is 4.98. It is diatomic in nature and when heated at 1700°C , it is converted into atomic form.



- It is slightly soluble in water and gives a light brown solution. Its solubility increases in water in presence of potassium iodide due to the formation of potassium triiodide. KI_3 easily breaks down and thus the solution has all the properties of free iodine.



- It is soluble in many organic solvents such as chloroform, carbon tetrachloride, alcohol, ether and carbon disulphide. The solution in CS_2 , CHCl_3 and CCl_4 is violet in colour.
- The most notable feature of I_2 solution in organic solvents is the dependence of their colour on the nature of the solvent. The solutions in aliphatic hydrocarbons such as CCl_4 violet and those in stronger donor solvents such as alcohols, ethers or amines is deep brown and those in aromatic hydrocarbons is light brown.

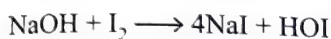
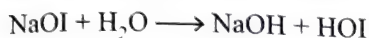
The variation in colour, can be explained in terms of a weak donor-acceptor interaction leading to complex formation between the solvent S (donor) and I_2 (acceptor). $\text{I}_2 \cdots \text{S}$. Such interactions are known as the "charge transfer" type and the complexes are known as charge transfer complexes. The violet colour of I_2 vapour is due to an excitation of an electron from $\pi^* \longrightarrow \sigma^*$ molecular orbital. In non-coordinating solvents, the transition energy is for

$\pi^* \rightarrow \sigma^*$ transition and hence the colour remains the same. However, in a donor solvent, the σ^* antibonding molecular orbital of I_2 acts as an electron acceptor and weakens the I-I bond. This alters the transition energy and leads to the appearance of new charge transfer band in the near UV spectrum (230–330 nm).

(B) Chemical properties

Iodine is chemically less reactive than chlorine and bromine.

- Reaction with alkalis:** Iodine reacts with cold dilute solution of NaOH forming hypoiodite. The colour of the solution becomes faint yellow. However, hypoiodite undergoes hydrolysis forming HOI.

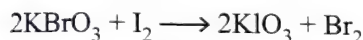
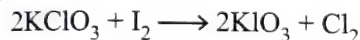


Hypoiodous acid

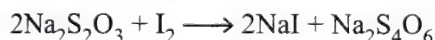
Iodine when heated with concentrated alkali solution, iodide and iodate are formed. The colour of iodine disappears.



- Iodine does not displace chlorine and bromine from chlorides and bromides, respectively but it displaces them from their oxy salts.



- Reaction with sodium thiosulphate:** Iodine solution is decolourised by sodium thiosulphate (hypo) as sodium tetrathionate and sodium iodide are formed. Both are colourless and soluble.

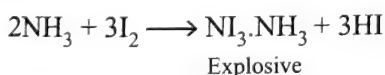


Sodium thiosulphate

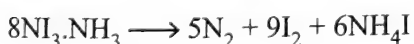
Sodium tetrathionate

This reaction is involved in iodometric titrations in presence of starch indicator.

- Reaction with NH_3 :** Iodine forms a mild explosive with ammonia.



Explosive

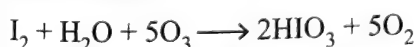


- Reaction with strong oxidising agents:** Strong oxidising agents convert iodine to iodic acid (HIO_3).

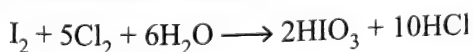
- With conc. HNO_3 :



- With ozone:



- With chlorine water:



Uses:

- It is used in medicine, e.g., tincture of iodine [1/2 oz. iodine, 1/4 oz. KI and 1 pint rectified spirit] and iodox as antiseptic and analgesic. Solutions of iodine in KI are used in the treatment of goitre.

- In the preparation of iodoform, iodides, dyes, etc.

- In analytical chemistry.

- In the preparation of photosensitive papers, films and plates.

4.11 HALOGEN ACIDS OR HYDRACIDS

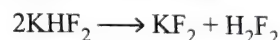
All the halogens combine with hydrogen and form covalent hydrides of the type HX , where $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I . These hydrides are known as halogen acids or hydracids.

Halogen acid	HF	HCl	HBr	HI
Name	Hydrogen fluoride	Hydrogen chloride	Hydrogen bromide	Hydrogen iodide

Preparation:

Hydrogen fluoride: It is an associated molecule and is represented by formula, H_2F_2 .

Pure anhydrous hydrogen fluoride is obtained by heating potassium hydrogen fluoride (dry) in a platinum retort.

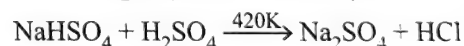


The vapours are condensed in a platinum condenser and collected in a platinum receiver. In place of platinum, lead apparatus can also be used.

The aqueous solution of H_2F_2 can be obtained by heating calcium fluoride with 90% conc. sulphuric acid in a lead retort.

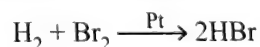
Hydrogen chloride:

- In laboratory, HCl can be prepared by heating a mixture of sodium chloride and conc. H_2SO_4 .

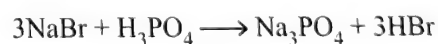


Hydrogen bromide:

- By direct combination of elements: HBr can be prepared by passing a mixture of H_2 and Br_2 over a platinum spiral heated to redness by an electric current.



- By heating bromide with conc. orthophosphoric acid.

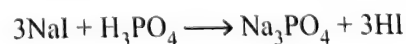


Hydrogen iodide:

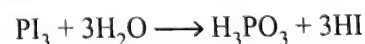
- HI can be prepared in small quantities by passing hydrogen and iodine vapours over red hot fine platinum.



- By heating iodides with conc. orthophosphoric acid.



- By hydrolysis of corresponding phosphorous trihalide.

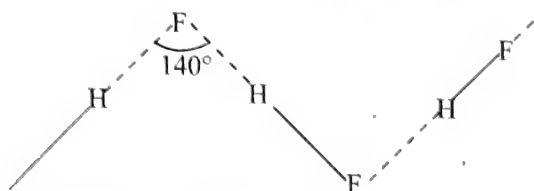


Properties:

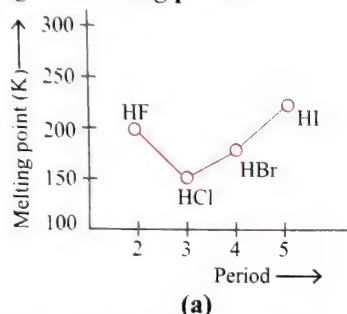
- Physical state:** Except hydrogen fluoride, other halogen halides are gases. They fume as air and have pungent odour.

These are colourless. All are heavier than air and can be liquefied to colourless liquids.

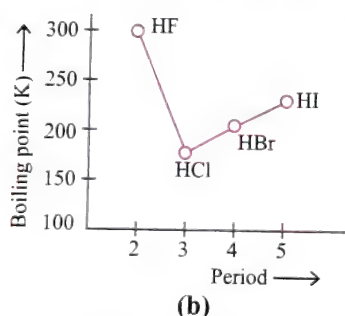
Hydrogen fluoride is a low boiling liquid (b.p. 293 K). The anomalous behaviour of HF is due to the presence of intermolecular hydrogen bonding in its molecules. Consequently, it exists as an associated molecule $(\text{HF})_n$. In the solid state, $(\text{HF})_n$ has the zig-zag structure.



2. a. Melting and boiling points:



[Melting point: $\text{HI}(222) > \text{HF}(190) > \text{HBr}(185) > \text{HCl}(159) \text{ K}$]



$\text{HF}(293) > \text{HI}(283) > \text{HBr}(206) > \text{HCl}(189) \text{ K}$

Fig. 4.1 (a) and (b) Melting and boiling points of hydrides of group 17

Explanation of m.pt. and b.pt. of hydrides of group 17	
Melting point	Boiling point
The melting point of HF is slightly lower than that of HI, due to increased molecular mass of HI which increases the van der Waals forces of attraction.	The boiling point of HF is highest as usual due to the strong H-bonding of HF in the liquid or gaseous state than in the solid state.
OR	
H-Bonding in HF is weaker in the solid state than in liquid or gaseous state.	

b. Comparison of the melting point and boiling point of NH_3 , H_2O and HF:

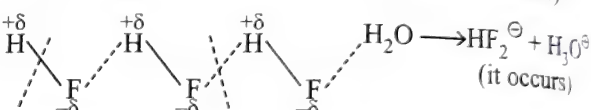
Melting point	Boiling point
$\text{H}_2\text{O}(273) > \text{NH}_3(195.2) > \text{HF}(190) \text{ K}$	$\text{H}_2\text{O}(373) > \text{HF}(293) > \text{NH}_3(238.5) \text{ K}$

$\text{EN of F} > \text{O} > \text{N}$, SO , HF should have stronger H-bonding. But both H_2O and NH_3 form four H-bonding while HF forms only two H-bonding. Moreover, the H-bonding in NH_3 is stronger in the solid state than in the liquid or gaseous state. Whereas the H-bond in HF is weaker in the solid state than in the liquid or gaseous state. Hence the m. pt. of $\text{H}_2\text{O} > \text{NH}_3 > \text{HF}$ as given above.

Both H_2O and NH_3 form four H-bonding while HF forms only two H-bonding. But H-bonding of HF in the liquid or gaseous state is stronger than in solid state. Therefore, the boiling point of $\text{HF} > \text{b.pt. of NH}_3$. Hence, the boiling point of $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$ as given above.

c. Existence of KHF_2 and non-existence of KHC l_2 , KHB r_2 or KH I_2 (dissociation):

In aqueous solution HF dissociates and gives the hydrogen difluoride in (HF_2) . This explains the existence of KHF_2 .



Whereas due to not so high electronegativity and large size of Cl , Br and I , the molecules of HCl , HBr and HI do not form H-bonding. This explains the non-existence of compounds such as KHC l_2 , KHB r_2 and KH I_2 .

3. Dipole moment:

With the increase in electronegativity of halogens down the group (\downarrow), the dipole moment of the hydrogen halides decreases

Dipole moment (μ): $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

4. Constant boiling mixture:

They are fairly soluble in water and form constant boiling mixtures with water called azeotrope.

Halogen acid	HF	HCl	HBr	HI
Composition	36%	20.4%	47%	57%
Boiling point ($^{\circ}\text{C}$)	120	110	126	127

5. Ionic character:

Down the group (\downarrow), with the decrease in electronegativity of halogen, the dipole moment of the halogen acid and hence the ionic character decreases.

% Ionic character: $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

6. Bond length:

With the increase in size of halogen atom, the bond length increases.

Bond length: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

7. Stability or bond strength:

Bond strength is inversely proportional to bond length. Hence, with the increase in bond length, bond strength decreases down the group (\downarrow)

Bond strength: $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

With the increase in bond length or with decrease in bond strength, bond dissociation enthalpy decreases.

Bond-dissociation enthalpy: $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

8. Thermal stability:

Thermal stability is directly proportional to the bond dissociation enthalpy. Since bond dissociation

enthalpy of HF is the highest and that of HI is the least, therefore, HF is the most stable halogen acid while HI is the least stable halogen acid.

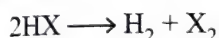
Thermal stability: $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

9. **Acid strength:** Hydrogen halides in the gaseous state are essentially covalent. In aqueous solution, however, they ionise and act as acids.

Thus, higher the bond dissociation enthalpy, lower is the degree of ionisation and hence weaker is the acid. Since the bond dissociation enthalpies of the halogen acids increase in the order: $\text{HI} < \text{HBr} < \text{HCl} < \text{HF}$, therefore, strength of the acids increases in the reverse direction, i.e., $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

Another reason for low acidity of HF as compared to other halogen acids is the strong H-bonding of F^\ominus ion to $\text{H}_3\text{O}^\oplus$ as compared to other halide ions.

10. **Reducing nature:** The reducing nature of a halogen acid depends upon the ease with which it decomposes to give H_2 and X_2 .



This, in turn, depends upon the bond dissociation enthalpy. Thus, greater the bond dissociation energy, more stable is the halogen acid and hence weaker is the reducing agent. Since the bond dissociation enthalpies of the halogen acids increase in the order: $\text{HI} < \text{HBr} < \text{HCl} < \text{HF}$, therefore, reducing nature of halogen acids increases in the reverse order: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

HF does not show any reducing nature. It cannot be oxidised even by strong oxidising agents. HI is the strongest reducing agent. Its aqueous solution gets oxidised even by atmospheric oxygen.

HCl can be oxidised by strong oxidising agents like

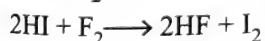
MnO_2 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, PbO_2 , Pb_3O_4 etc.

HBr acts as stronger reducing agent than HCl. It can be oxidised by H_2SO_4 and atmospheric oxygen.

HI is the strongest reducing agent.

It reduces H_2SO_4 to SO_2 , S to H_2S , nitric acid to NO_2 , nitrous acid to NO , FeCl_3 to FeCl_2 , cupric salt to cuprous salt, etc.

11. **Action of halogens:** F_2 can displace Cl_2 , Br_2 and I_2 from HCl , HBr and HI .



Cl_2 can displace Br_2 and I_2 from HBr and HI and Br_2 can displace only I_2 from HI . Iodine can displace none.

12. **Reaction with ammonia:** HCl , HBr and HI combine with ammonia giving white fumes of ammonium halides.



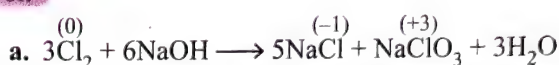
13. **Corrosive nature:** All the halogen acids, in particular, HF are corrosive and hence extreme care should be taken while working with them. Out of all the hydrohalic acids,

HF attacks glass and hence etching glass and manufacture of glass shell for television tubes.

ILLUSTRATION 4.3

- Write the balanced chemical equation for the reaction of Cl_2 with hot and concentrated NaOH . Is this reaction a disproportionation reaction?
- When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?
- Deduce the molecular shape of BrF_3 on the basis of VSEPR theory.

Sol.



Yes, chlorine from zero oxidation state is reduced to -1 and oxidised to $+3$ oxidation states.

- b. HCl reacts with Fe to produce H_2 gas.



Liberation of H_2 prevents the formation of ferric chloride, FeCl_3 .

- c. The central atom Br in BrF_3 has seven electrons in the valence shell. Three of these will form electron pair bonds with three fluorine atoms leaving behind four electrons. Thus, there are three bond pairs and two lone pairs. According to VSEPR theory, these will occupy the corners of trigonal bipyramid. The two lone pairs will occupy the equatorial positions to minimise lone pair and the bond pair–lone pair repulsions which are greater than the bond pair–bond pair repulsions. In addition, the axial fluorine atoms will be bent towards the equatorial fluorine in order to minimise the lone pair–lone pair repulsions. The shape would be of slightly bent T.

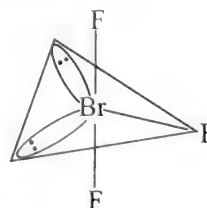


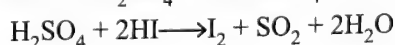
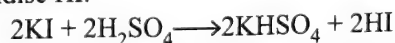
ILLUSTRATION 4.4

Explain the following:

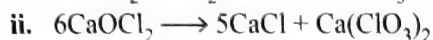
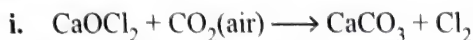
- In the preparation of HI from KI , phosphoric acid is preferred to sulphuric acid.
- Boiling point of HCl is lower than HF .
- Bleaching powder loses its bleaching property when kept in an open bottle for a long time.

Sol.

- a. Besides acidic nature of sulphuric acid, it acts as an oxidising agent. H_2SO_4 oxidises HI (reducing agent) formed from KI into iodine. Thus, H_3PO_4 is preferred as it does not oxidise HI .



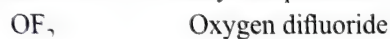
- b. In HF, there is hydrogen bonding. It is, therefore, an associated liquid. No hydrogen bonding is present in HCl. Only van der Waals' forces are present. This is the reason why boiling point of HCl is lower than HF.
- c. Bleaching action of bleaching powder is due to release of Cl_2 at the time of application. Chlorine is lost by bleaching powder on long standing in open by the following two processes.



Thus, CaCl_2 and $\text{Ca}(\text{ClO}_3)_2$ do not release Cl_2 at the time of use. Hence, bleaching property is lost by bleaching powder on exposure for long time.

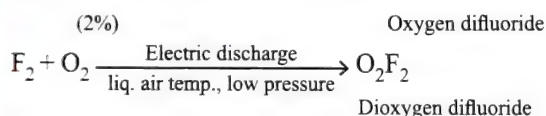
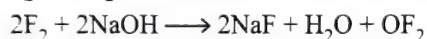
4.12 OXIDES OF FLUORINE

Fluorine forms two binary compounds with oxygen, i.e.

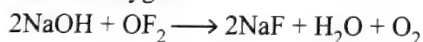


OF_2 is thermally stable at 298 K while O_2F_2 is highly unstable and decomposes into its elements even at 178 K.

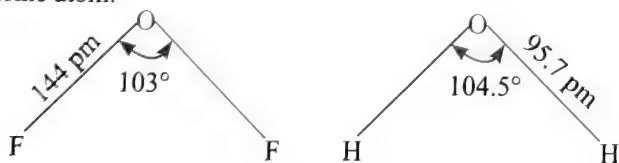
Preparation: Oxygen difluoride (OF_2) is prepared by passing F_2 through 2% NaOH solution while O_2F_2 (dioxygen difluoride) is obtained by passing electric discharge through a mixture of F_2 and O_2 under low pressure and at liquid air temperature.



OF_2 dissolves in water and gives a neutral solution, therefore, it is not an acid anhydride. It dissolves in NaOH to give sodium fluoride and dioxygen.

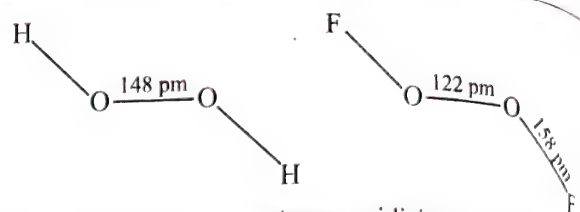


Structure: The structure of OF_2 is similar to that of H_2O while that of O_2F_2 is similar to that of H_2O_2 involving sp^3 hybridisation of O-atoms. However, due to greater electronegativity of fluorine as compared to oxygen, the bond pairs in OF_2 lie nearer to the fluorine atom.



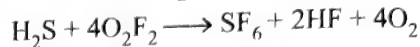
In contrast, in H_2O , due to greater electronegativity of O as compared to H, the bond pairs lie nearer the O atom. Consequently, bond pair-bond pair repulsion in H_2O is more than bond pair-bond pair repulsion in OF_2 and hence F—O—F bond angle is less (103°) than H—O—H bond angle (104.5°).

Further, as F is more electronegative than O, it attracts the lone pairs of electrons on the O atom towards itself. Therefore, lone pair-lone pair repulsion between the two O atoms in O—O bond is much lower in O_2F_2 than in H_2O_2 . In other words, the O—O bond length in O_2F_2 is much shorter (122 pm) than that in H_2O_2 (148 pm). However, the O—F bond lengths in O_2F_2 are much longer (158 pm) than in OF_2 (141 pm).



Uses: Both OF_2 and O_2F_2 are strong oxidising and fluorinating agents. O_2F_2 oxidises plutonium (Pu) to PuF_6 and this reaction is used in removing Pu as PuF_6 from spent nuclear fuel.

O_2F_2 also oxidises H_2S to SF_6 .



Being a strong oxidising agent, OF_2 has been used as a rocket fuel.

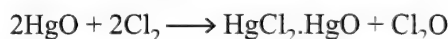
4.13 OXIDES OF CHLORINE

Oxidation state	Oxide of chloride	Name
+1	Cl_2O	Dichlorine monoxide
+4	ClO_2	Chlorine dioxide
+6	Cl_2O_6	Chlorine hexoxide
+7	Cl_2O_7	Chlorine heptoxide

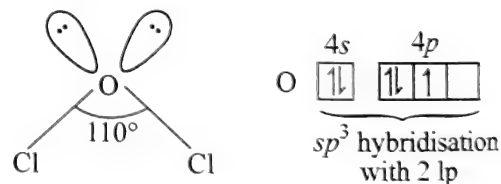
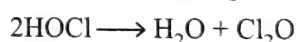
4.13.1 CHLORINE MONOXIDE, Cl_2O

Preparation:

- By passing dry Cl_2 (diluted with dry air) over freshly precipitated yellow oxide of Hg, i.e., HgO , previously ignited to $300\text{--}400^\circ\text{C}$ and contained in a cooled tube.



- By distilling an aqueous solution of hypochlorous acid (HOCl) at reduced pressure.

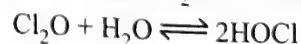


Geometry: Tetrahedral,

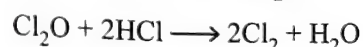
Shape: Bent or V-shaped molecule.

Properties:

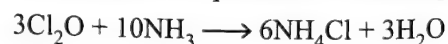
- Brownish yellow gas which condenses to orange coloured liquid (boiling point 273 K).
- It dissolves in water, giving a golden yellow solution of hypochlorous acid. It is therefore, also known as anhydride of HOCl . Solubility of Cl_2O in H_2O is very high (14.4 g/100 g of H_2O at -9°C).



- It acts as strong oxidising agent, which is decomposed by HCl , or oxidises HCl to Cl_2 .



- Cl_2O explodes in the presence of reducing agents or NH_3 .



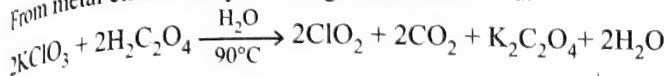
Uses:

1. For bleaching highest grade paper pulp.
2. In water purification and for odour control.
3. In making wool unshrinkable.
4. For improving the quality of low grade fats and oils.

4.13.2 CHLORINE DIOXIDE, ClO_2

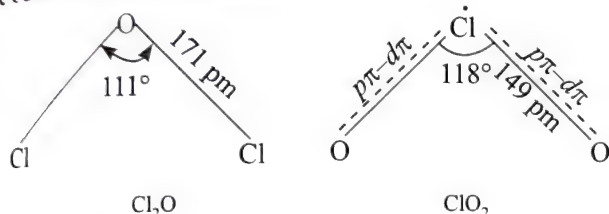
Preparation:

From metal chlorate by reacting with oxalic acid.



Advantage of this method: CO_2 formed acts as diluent for the extremely explosive ClO_2 and thus this method is safest method for laboratory preparation of ClO_2 .

Structures: In ClO_2 , the central Cl atom is sp^2 -hybridised with $\text{O}-\text{Cl}-\text{O}$ angle of 118° . Both the $\text{Cl}-\text{O}$ bonds have equal (149 pm) bond lengths and are quite shorter than those in Cl_2O (171 pm). Therefore $\text{Cl}-\text{O}$ bond has appreciable double bond character due to $p\pi-d\pi$ bonding. The molecule is paramagnetic since it has one odd electron in a p -orbital.



Odd electron molecules often dimerise in order to pair the electrons but ClO_2 does not. This is probably due to the reason that odd electron is delocalised. In contrast, the odd electron on N in NO is localised and hence NO readily dimerises to form $(\text{NO})_2$.

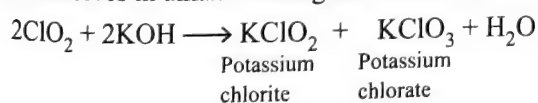
Properties:

1. Dark yellow pungent smelling gas which can be condensed to dark red liquid, boiling point 284 K and frozen to yield orange-red crystals (at 194 K).
2. Liquids and gas are fairly stable in dark, but decompose in light. The gas or liquid explodes violently on heating ($> -40^\circ\text{C}$) giving a mixture of Cl_2 , O_2 , Cl_2O_6 and Cl_2O .
3. It reacts with water to give a mixture of chlorous acid and chloric acid.

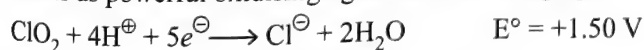
$$\begin{matrix} (+4) & & (+3) & & (+5) \\ 2\text{ClO}_2 + \text{H}_2\text{O} \longrightarrow & \text{HClO}_2 + & \text{HClO}_3 \end{matrix}$$

chlorous acid chloric acid.

4. It dissolves in alkali forming chlorite and a chlorate, e.g.



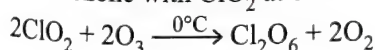
5. It acts as powerful oxidising agent and bleaching agent.



6. With O_3 : $2\text{ClO}_2 + 2\text{O}_3 \xrightarrow{0^\circ\text{C}} \text{Cl}_2\text{O}_6 + 2\text{O}_2$

4.13.3 CHLORINE HEXOXIDE, Cl_2O_6 ($\text{Cl}_2\text{O}_6 \rightleftharpoons 2\text{ClO}_3$)

Preparation:

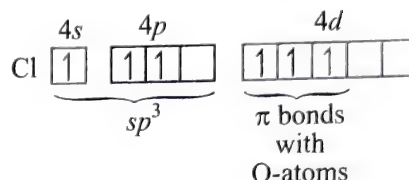
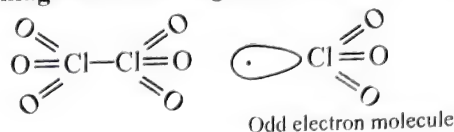
Reaction of ozone with ClO_2 at 0°C .

Properties and structure:

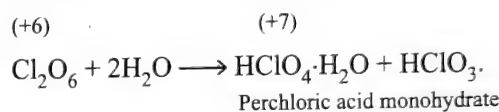
1. Cl_2O_6 appears to dissociate to monomer under certain conditions.



Pure liquid is diamagnetic, suggesting that most of the species present are Cl_2O_6 molecules. **Vapour, however, is paramagnetic** indicating the formation of monomer, ClO_3 .



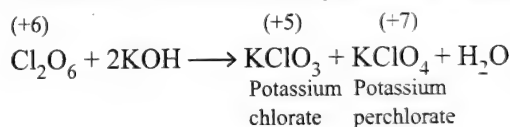
2. It is red, explosive, oily liquid which freezes at 276.5 K. It dissociates on heating and eventually breaks to elements.
3. It reacts violently with water, but with cooled water vapour, $\text{HClO}_4 \cdot \text{H}_2\text{O}$ and HClO_3 are produced.



(Disproportionation)

That is, it is a mixed anhydride of perchloric acid and chloric acid.

4. It dissolves in alkali forming chlorate and perchlorate.



5. It is a strong oxidising agent and explodes in contact with grease.

6. With HF: $\text{Cl}_2\text{O}_6 + \text{HF} \rightleftharpoons \text{HClO}_4 + \text{ClO}_2\text{F}$
- Chloryl fluoride

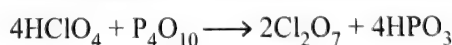
7. With N_2O_4 : $\text{Cl}_2\text{O}_6 + \text{N}_2\text{O}_4 \rightleftharpoons \text{ClO}_2 + [\text{NO}_2]^+ [\text{ClO}_4]^-$

8. In solid state Cl_2O_6 exist as $[\text{ClO}_2]^+ [\text{ClO}_4]^-$
- $sp^2 (< 120^\circ)$ $sp^3 (109^\circ, 28^\circ)$

4.13.4 CHLORINE HEPTOXIDE, Cl_2O_7

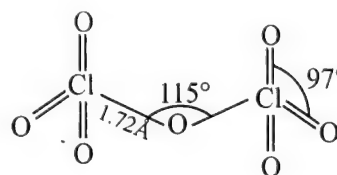
Preparation:

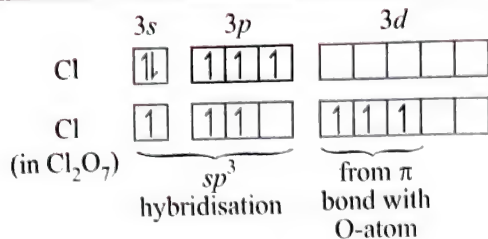
1. By dehydration of perchloric acid with P_4O_{10} at 263 K.



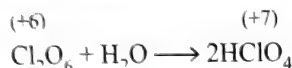
Cl_2O_7 may be distilled off under reduced pressure, with precaution against explosions.

Structure:

Molecule Cl_2O_7 is polar, $\mu = 0.72$

**Properties:**

1. It is a colourless, oily liquid (boiling point 355 K) which is extremely explosive in nature. It explodes on heating or on percussion.
2. It is moderately stable liquid.
3. Slowly reacts with water forming HClO₄ i.e. it is perchloric anhydride.

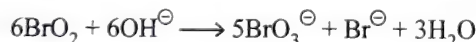
**4.14 OXIDES OF BROMINE**

The bromine oxides Br₂O, BrO₂ and BrO₃ are the least stable halogen oxides (middle row anomaly) and exist only at low temperatures. They are very powerful oxidising agents. Their structures are similar to those of chlorine oxides having comparable molecular formulae.

Br₂O is a dark brown solid, moderately stable at 213 K. It is highly oxidising and converts I₂ to I₂O₅, benzene to 1,4-diquinone.

Br₂O is a pale yellow crystalline solid, which is stable only at < 233 K and decomposes violently into its elements at 273 K.

On alkaline, hydrolysis gives bromide and bromate.



BrO₃ is obtained when Br₂ is treated with O₃ at 273 K. BrO₃ is a white solid which is unstable above 193 K.

4.15 OXIDES OF IODINE

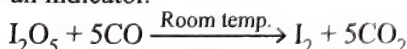
Iodine forms three oxides, I₂O₄, I₂O₅ and I₄O₉. Out of these, I₂O₅ is the most stable. It is the only true oxide of iodine while others are regarded as iodates of tripositive iodine, i.e., I₂O₄ is probably [IO][⊕] [IO₃][⊖] and I₄O₉ is probably I³⁺ (IO₃[⊖])₃.

Preparation: I₂O₅ is obtained by dehydrating iodic acid at 473 K.

$$2\text{HIO}_3 \xrightarrow{473\text{K}} \text{I}_2\text{O}_5 + \text{H}_2\text{O}$$

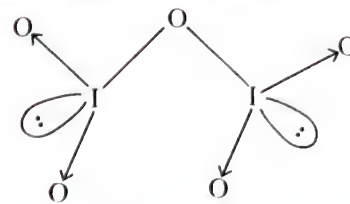
Therefore, it is the anhydride of iodic acid. It dissolves in water to produce iodic acid.

It is a strong oxidising agent and oxidises CO to CO₂ rapidly and quantitatively at room temperature, liberating I₂ which can be titrated against a standard solution of Na₂S₂O₃ using starch as an indicator.



Therefore, I₂O₅ is used for detection and estimation of CO in the atmosphere and other gaseous mixtures.

Structure: I₂O₅ consists of two IO₃ pyramidal units joined through a common oxygen atom. Each iodine has two I → O coordinate bonds, one I—O covalent bond and a lone pair of electrons.

**4.16 OXOACIDS OF HALOGENS**

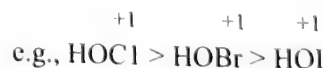
Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid. Chlorine, bromine and iodine form four series of oxoacids with formula HOX [halic (I) acid or hypohalous acid], HOXO [halic (III) acid or halous acid], HOXO₂ [halic (V) acid or halic acid] and HOXO₃ [halic (VII) acid or perhalic acid], although many of these are known only in solution or as salts. The names of some important oxoacids along with their oxidation states are given in Table 4.2.

Table 4.2 Oxoacids of halogens

Name / oxidation state	Fluorine	Chlorine	Bromine	Iodine
Halic (I) acid (Hypo-halous acid)	HOF (Hypo-fluorous acids)	HOCl (Hypochlorous acid)	HOBr (Hypobromous acid)	HOI (Hypoiodous acid)
Halic(III) acid (Halous acid)	—	HClO ₂ (Chlorous acid)	—	—
Halic(V) acid (Halic acid)	—	HClO ₃ (Chloric acid)	or HBrO ₃ (Bromic acid)	HIO ₃ (Iodic acid)
Halic(VII) acid (Perhalic acid)	—	HClO ₄ (Perchloric acid)	HBrO ₄ (Perbromic acid)	HIO ₄ (Periodic acid)

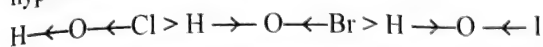
Acid strength and oxidising power of oxoacids of halogens:

1. **Acid strength of hypohalous acids:** Acid strength of oxoacids of different halogens having same oxidation state decreases with the increase in atomic number, or decrease in electronegativity of the halogen.

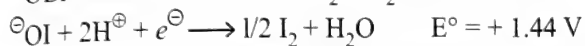
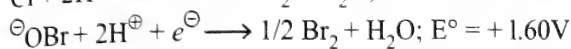
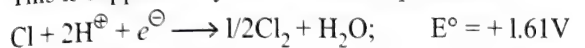


Explanation: This can be explained on the basis of electronegativity of the halogen atom. Oxygen is more electronegative than the halogen (Cl, Br or I), therefore, it attracts the electrons of the oxygen–halogen bond towards itself. Now, as the electronegativity of the halogen decreases from Cl to I, the shared pair of electrons of the oxygen–halogen bond moves closer and closer towards the oxygen atom. Consequently, electron-density on the oxygen atom increases from Cl to I. In other words, O atom in H—O—Cl has the lowest electron density while it has the highest in H—O—I.

Consequently, O in $\text{H}-\text{O}-\text{Cl}$ attracts the electrons of $\text{O}-\text{H}$ bond towards itself most strongly followed by in $\text{H}-\text{O}-\text{Br}$ and least strongly in $\text{H}-\text{O}-\text{I}$. As a result, $\text{O}-\text{H}$ breaks most readily in $\text{H}-\text{O}-\text{Cl}$ and least easily in $\text{H}-\text{O}-\text{I}$. In other words, the acid strength of the hypohalous acids decreases in the order:



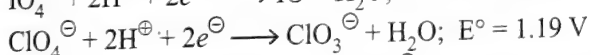
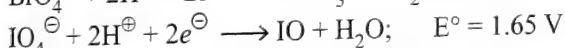
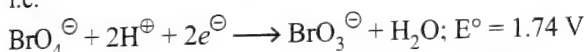
- b. **Oxidising power of hypohalous acids:** As the size of the halogen increases, the thermal stability of the $\text{O}-\text{X}$ bond increases and the oxidising power of the hypohalous acid or the hypohalite ion decreases. Thus, hypochlorites are stronger oxidising agents than hypoiodites. Surprisingly, hypobromite ions and hypochlorite ions are equally strong oxidising agents. This is supported by their electrode potentials:



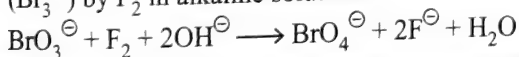
2. a. **Acid strength of perhalic acids:** As the electronegativity of the halogen decreases, the tendency of the XO_3 group to withdraw electrons of the $\text{O}-\text{H}$ bond towards itself decreases and hence the acid strength of the perhalic acid decreases in the same order, i.e., $\text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$.

- b. **Oxidising power of perchlorates:** Perchlorates are strong oxidising agents, their oxidising power decreases in the order: $\text{BrO}_4^- > \text{IO}_4^- > \text{ClO}_4^-$

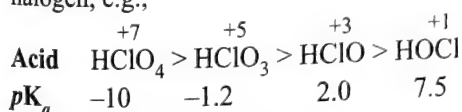
Explanation: This order can be explained on the basis of their electrode potentials for the following reactions, i.e.



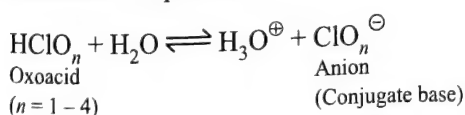
Although among perchlorates, BrO_4^- is the strongest oxidising agent, yet it is a weaker oxidising agent than F_2 . It is because of this reason that perbromates and perbromic acid can be obtained by oxidation of bromates (Br_3^-) by F_2 in alkaline solution.



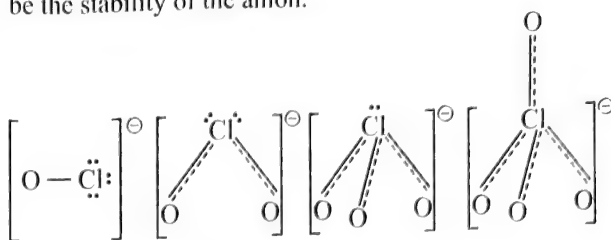
3. **Acid strength of oxoacids of the same halogen in different oxidation states:** Acid strength of oxoacids of the same halogen increases with increase in oxidation number of the halogen, e.g.,



Explanation: This can be explained on the basis of the relative stability of the anion (or the conjugate base) left after removal of a proton.



Now greater the number of oxygen atoms in the anion (conjugate base), greater will be the dispersal of the negative charge through $p\pi-d\pi$ back bonding and hence greater will be the stability of the anion.



Stability of the ion increases

Since the stability of the anions decreases in the order: $\text{ClO}_4^- > \text{ClO}_3^- > \text{ClO}_2^- > \text{ClO}^-$

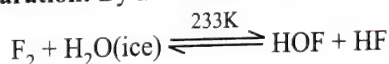
Hence, their acid strength also decreases in the same order: $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$

Further, as the stability of the anion increases, its oxidising power decreases accordingly. In other words, the oxidising power of the oxoacids of chlorine increases in the reverse order of their acid strength,

i.e., $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HOCl}$

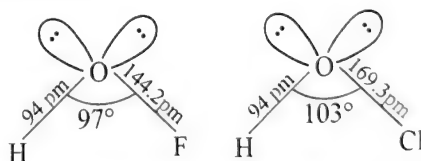
4.16.1 HYPOFLUOROUS ACID, HOF

Preparation: By fluorination of ice



HOF thus prepared is immediately removed from the reaction mixture otherwise it will be decomposed by HF , F_2 or H_2O .

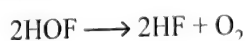
Structure: In HOF, oxidation state of F is +1. The oxygen atom in HOF like that in HOCl is sp^3 -hybridised. However, due to higher electronegativity of F over Cl, the bond pair-bond pair repulsions of $\text{H}-\text{O}$ and $\text{O}-\text{F}$ bonds in HOF are less than those of $\text{H}-\text{O}$ and $\text{O}-\text{Cl}$ bonds in HOCl .



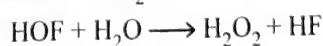
Consequently, bond angle in HOF is less than HOCl . As expected due to bigger size of Cl over F, the $\text{O}-\text{Cl}$ bond is much longer than the $\text{O}-\text{F}$ bond. But the $\text{O}-\text{H}$ bonds in both these molecules have approximately the same length.

Properties:

1. HOF is highly unstable and rapidly decomposes at room temperature to form HF and O_2 with a half life of 9.30 minutes.



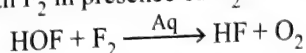
2. It reacts with H_2O to form HF and H_2O_2 .



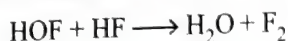
In other words, it does not ionise in water and hence the corresponding salts, i.e., hypofluorite ions (^-OF) are not known.



3. HOF cannot be dehydrated to form OF_2 , hence, OF_2 cannot be regarded as an anhydride of HOF. However, HOF reacts with F_2 in presence of H_2O to form OF_2 .



4. HOF reacts with HF to form $\text{H}_2\text{O} + \text{F}_2$



4.16.2 OXOACIDS OF CHLORINE

Oxidation State	Oxide of chloride	Name
+1	HOCl	Hypochlorous acid
+3	HOCl_2	Chlorous acid
+5	HClO_3	Chloric acid
+7	HClO_4	Perchloric acid

4.16.2.1 Hypochlorous Acid (HOCl)

Preparation:

- By passing Cl_2 gas into water

$$\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{HCl} + \text{HOCl}$$

(0) (-1) (+1)
- By shaking Cl_2 water with freshly precipitated yellow HgO .

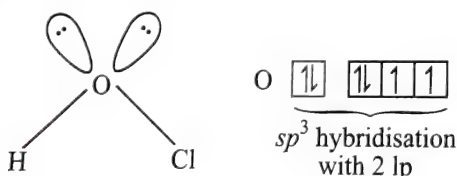
$$2\text{HgO} + 2\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{HgCl}_2 \cdot \text{HgO} \downarrow + 2\text{HOCl}$$

Oxychloride of mercury (Hg_2OCl_2)
- By passing Cl_2 through a suspension of CaCO_3 in water.

$$\text{CaCO}_3 + \text{H}_2\text{O} + 2\text{Cl}_2 \longrightarrow \text{CaCl}_2 + \text{CO}_2 + 2\text{HOCl}$$
- Commercially, it is prepared by passing CO_2 into a suspension of bleaching powder, CaOCl_2 in water and then distilling:

$$2\text{CaOCl}_2 + \text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{CaCl}_2 + \text{CaCO}_3 + 2\text{HOCl}$$

Structure:



Properties:

- Strong or concentrated solution of HOCl is yellow in colour (because of dissolved Cl_2) while dilute solution is colourless.
- Highly unstable and decomposes into HCl and O_2 .

$$2\text{HOCl} \longrightarrow 2\text{HCl} + \text{O}_2$$
- Reacts with Mg to liberate H_2 .

$$2\text{HOCl} + \text{Mg} \longrightarrow \text{Mg}(\text{OCl})_2 + \text{H}_2$$
- On distillation, decomposes to give H_2O and Cl_2O .

$$2\text{HOCl} \longrightarrow \text{Cl}_2\text{O} + \text{H}_2\text{O}$$
- Acts as powerful oxidising and bleaching agent

$$\text{HOCl} \longrightarrow \text{HCl} + \text{O}$$

or $\text{ClO}^\ominus + 2\text{H}^\oplus + 2e^\ominus \longrightarrow \text{Cl}^\ominus + \text{H}_2\text{O}$
- In alkaline solution, oxidises chromic hydroxide to chromate.

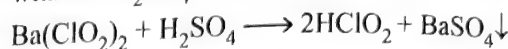
$$2\text{Cr}(\text{OH})_3 + 2\text{NaClO} + 4\text{NaOH} \longrightarrow 2\text{Na}_2\text{CrO}_4 + 3\text{NaCl} + 5\text{H}_2\text{O}$$

4.16.2.2 Chlorous Acid, HClO_2

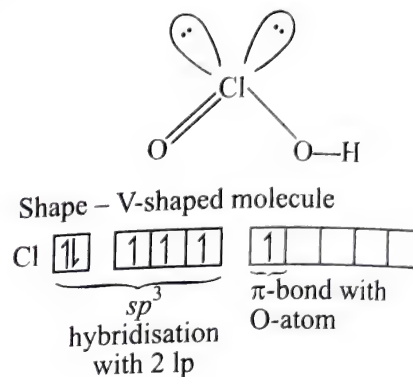
Preparation:

- Free chlorous acid (halous acids) have not been isolated (as they are weak acids).

An aq. solution of HClO_2 is obtained by treating $\text{Ba}(\text{ClO}_2)_2$ with dil. H_2SO_4 .



Structure:



Properties:

- Chlorous acid liberates iodine from iodides and thus acts as an oxidising agent.

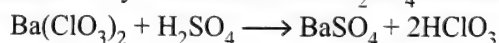
$$4\text{KI} + \text{NaClO}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{KOH} + \text{NaCl} + 2\text{I}_2$$
- It undergoes autooxidation at ordinary temperature and change into a mixture of HOCl and HClO_3 .

$$2\text{HClO}_2 \longrightarrow \text{HOCl} + \text{HClO}_3$$

(+3) (+1) (+5)
- Possess bleaching property.
- Freshly prepared solution is colourless, but it soon decomposes to ClO_2 , which colour the solution yellow.

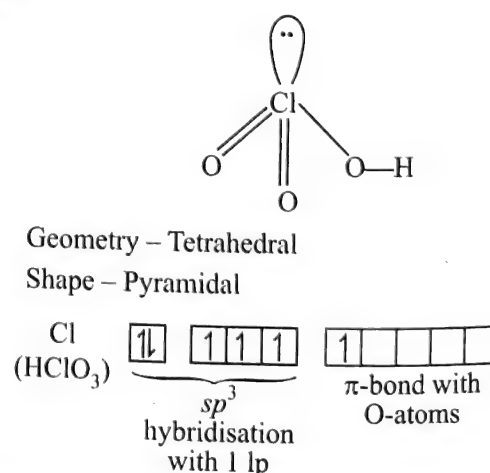
4.16.2.3 Chloric Acid, HClO_3

Preparation: By the action of dil. H_2SO_4 on barium chlorate



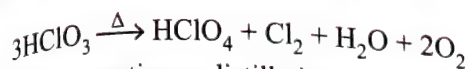
BaSO_4 is filtered off and unused BaSO_4 is precipitated by Baryta water, filtrate is evaporated on vacuum dessicator over conc. BaSO_4 , until 40% solution of HClO_3 is obtained.

Structure:

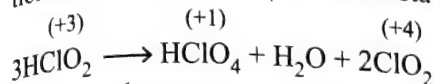


Properties:

- Conc. HNO_3 is colourless, pungent smelling liquid fairly stable in dark. But undergoes decomposition on exposure to light.



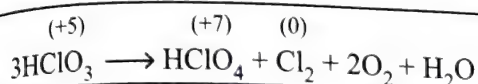
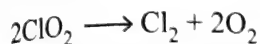
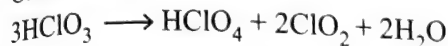
2. On evaporation or distillation, HClO_3 undergoes disproportionation to give HClO_4 , the most stable oxyacid of Cl_2 .



3. Organic substances, e.g. paper, cotton, wool catch fire in contact with acid.

4. Acts as powerful oxidising and bleaching agent.

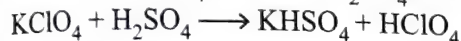
On heating,



4.16.2.4 Perchloric Acid, HClO_4

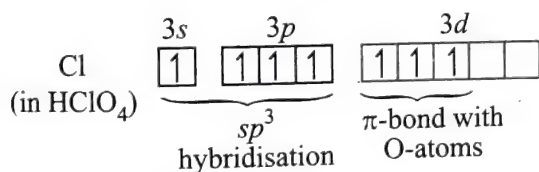
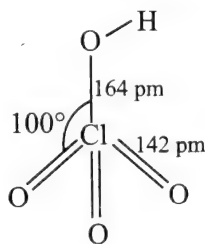
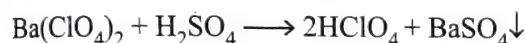
Preparation:

1. Anhydrous perchloric acid may be obtained by distilling a mixture of KClO_4 and conc. H_2SO_4 under reduced pressure.



The distillate is yellow in colour owing to the presence of ClO_2 and HCl as impurities which are removed by blowing air through it.

2. By treating $\text{Ba}(\text{ClO}_4)_2$ with dil. H_2SO_4 and removing the insoluble BaSO_4 by filtration.



Properties:

- Colourless, hygroscopic oily liquid (boiling point 292 K) which fumes in moist air.
- It is unstable and decomposes on standing for few days even in dark, on heating, it decomposes with explosion.
- It produces severe wound on the skin. On dehydration with P_4O_{10} , yields Cl_2O_7 .

$$4\text{HClO}_4 + \text{P}_4\text{O}_{10} \longrightarrow 2\text{Cl}_2\text{O}_7 + 4\text{HPO}_3$$

ILLUSTRATION 4.5

Explain the following:

- More metal fluorides are ionic in nature than metal chlorides.
- Perchloric acid is a stronger acid than sulphuric acid.
- Fluorine does not undergo disproportionation reactions but other halogens do.

Sol.

- According to Fajan's rules, a bigger anion is more easily polarised than a smaller anion by the same metal cation. F^\ominus ion is smaller in size in comparison to Cl^\ominus ion. Thus, the metal fluoride is more ionic than the metal chloride for the same metal cation.
- The oxidation state of chlorine in HClO_4 is +7 while that of S in H_2SO_4 is +6. This O—H bond in HClO_4 is easily broken than in H_2SO_4 . Hence, HClO_4 is a stronger acid in comparison to H_2SO_4 .
- F being the most electronegative element shows only -1 oxidation/state while other halogens show both negative (-1) and positive (+1, +3, +5, +7) oxidation states. Thus, fluorine does not show disproportionation reactions but other halogens do.

ILLUSTRATION 4.6

- Fluorine does not form oxyacid, but other halogens do. Why?
- Both NO and ClO_2 are odd electron species. NO dimerises but ClO_2 does not. Why?

Sol.

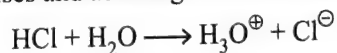
- In oxy-acids, the central element always exhibits positive oxidation states. Fluorine, being the most electronegative, never shows positive oxidation states, hence F does not form oxy-acids. Other halogens have the tendency to show positive oxidation states and hence form oxy-acids.
- In NO, the size of nitrogen atom is small and the odd electron is attracted by only one oxygen atom while in ClO_2 , the size of chlorine atom is comparatively large and an odd electron is attracted by two oxygen atoms. As a result, the odd electron on N in NO is localised while the odd electron on chlorine in ClO_2 is delocalised. Thus, NO has a tendency to dimerise but ClO_2 does not.

ILLUSTRATION 4.7

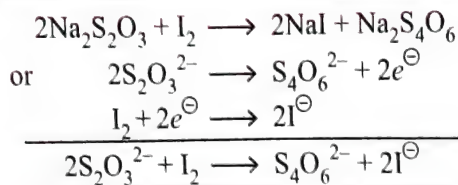
- Fluorine cannot be prepared from fluorides by chemical oxidation. Why?
- Anhydrous HCl is bad conductor of electricity while aqueous HCl is a good conductor. Give reason.
- Fresh iodine stain can be removed by washing with hypo solution. Explain.

Sol.

- The standard reduction potential of fluorine is maximum. Thus, it cannot be oxidised by any other reagent. Fluoride ion is very stable due to small size and high electronegativity of fluorine atom. Thus fluorine cannot be prepared from fluorides by chemical oxidation.
- In anhydrous state, HCl is a covalent molecule, hence bad conductor of electricity. Whereas, in aqueous state, HCl ionises and acts as good conductor.



- Hypo solution, i.e. sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ reacts with iodine to form water soluble colourless sodium tetrathionate and sodium iodide.



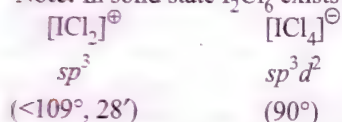
4.17 INTERHALOGEN COMPOUNDS

(AX_n, where X = 1, 3, 5 or 7)

Due to difference in electronegativity, the halogen atoms combine with each other and gives rise to formation of binary covalent compounds called **interhalogen compounds**. In terms of composition, an interhalogen compound has one of the following stoichiometry.

	Oxidation state of A	Cl	Br	I
AX	+1	ClF	BrF, BrCl	(IF), ICl, IBr
AX ₃	+3	ClF ₃	BrF ₃	IF ₃ , I ₂ Cl ₆
AX ₅	+5	ClF ₅	BrF ₅	IF ₅
AX ₇	+7	—	—	IF ₇

Note: In solid state I₂Cl₆ exists as:

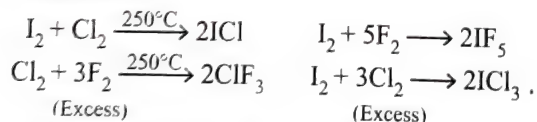


A central atom is larger than B, i.e., A has less electronegativity than B. Interhalogen compounds are named as halides of less electronegative atom e.g. ClF is chlorine monofluoride rather than fluorine monochloride.

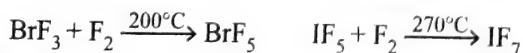
AX_n: Number of substituents A depends on the size of A as well as that of X. Thus, the bigger the size of A, the larger the number of X atoms it can carry, while the smaller the size of X, more of these can be accommodated around a given A atom.

Preparation:

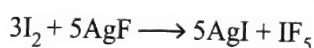
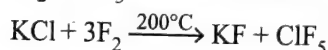
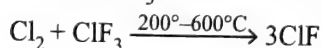
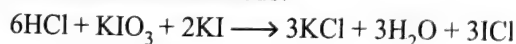
- By direct combination of the elements:** However, the product formed by direct interaction of elemental halogens depends upon the conditions under which the reaction is carried out.



- From lower interhalogens:** By reacting lower interhalogens with halogens. This method is particularly used for the preparation of halogen fluorides, e.g.



- Miscellaneous methods:**

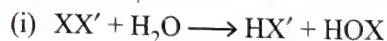


Properties:

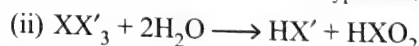
- Physical state:** Interhalogen compounds may be covalent gases (ClF, BrF, ClF₃, IF₇), liquids (BrF₃, BrF₅, IF₅) or solids (ICl, IBr, IF₃, ICl₃).
- Colour:** Although many interhalogen compounds of F are colourless those having heavier halogens are coloured. The colour becomes deeper with an increase in atomic weight of the compound.
- Diamagnetic nature:** Since all the valence electrons are present as bonding or non-bonding (lone pairs) electron pairs, these compounds are diamagnetic in nature.
- Heat of formation:** It is of low magnitude. These are extremely volatile compounds. In general compounds containing fluorine are more volatile than those containing Cl, Br or I.
- Boiling point:** For each type of interhalogen compound, the boiling point increases with increase in electronegativity difference between A and X.
- Thermal stability:** For AX type, thermal stability decreases with decrease in electronegativity difference between A and X. IF (1.5) > BrF (1.2) > ClF (1.0) > ICl (0.5) > IBr (0.3) > BrCl (0.2).

The greater the electronegativity difference, more polar is the A—X bond and hence greater the thermal stability.

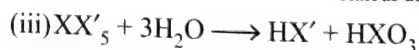
- Reactivity:** In general interhalogen compounds are more reactive than halogens (except F₂). This is because (X—X) bond in interhalogens is weaker than (X—X) bond in halogens except F—F bond.
- Hydrolysis:** All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX'), halite (when XX'₃), halate (when XX'₅) and perhalate (when XX'₇) anion derived from larger halogen:



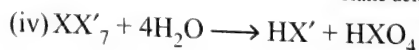
Hypohalous acid



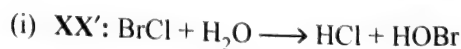
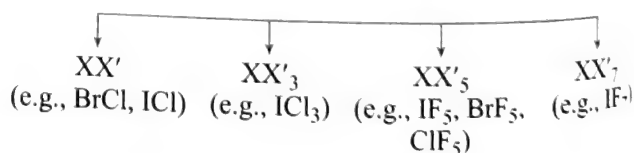
Halous acid



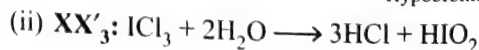
Halic acid



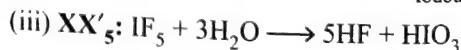
Per-halic acid



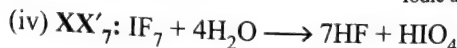
Hypobromous acid



Iodous acid

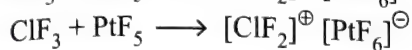
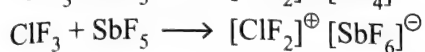
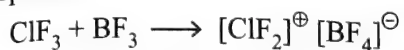


Iodic acid

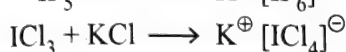
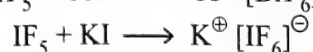
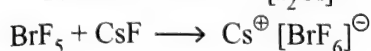
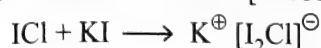
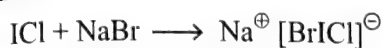


Periodic acid

Interhalogen compounds reacts with F^{\ominus} acceptor to form cationic species.



9. Interhalogens also form addition compounds with alkali halides. These compounds are ionic, and are called polyhalides.

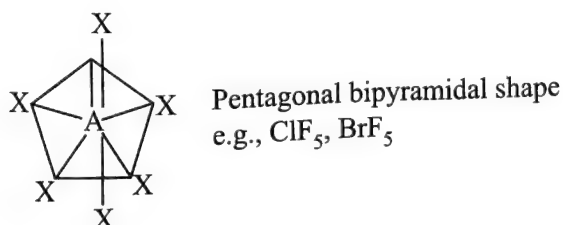
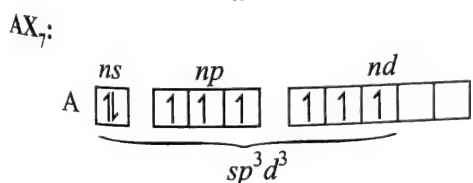
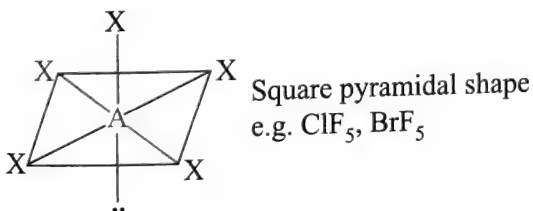
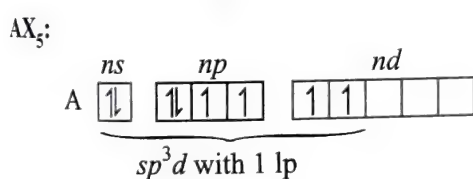
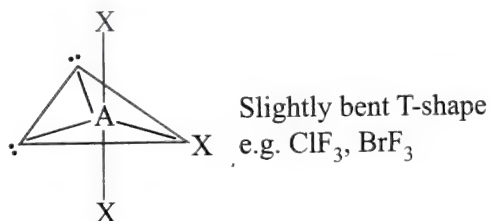
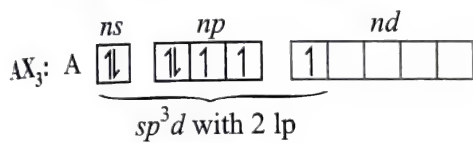
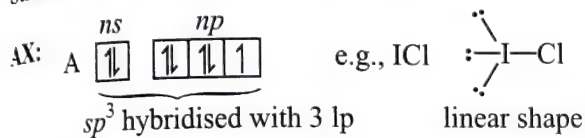


10. As non-aqueous ionising solvents:



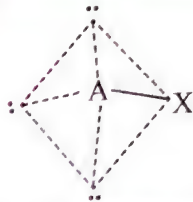
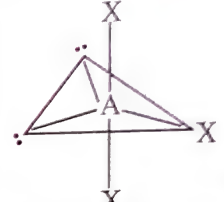
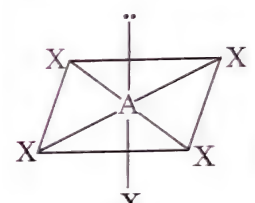
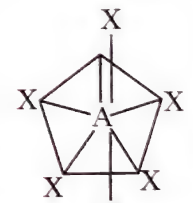
Thus substances producing $[BrF_2]^{\oplus}$ ions are acids and $[BrF_4]^{\ominus}$ ions are bases in BrF_3 (solvent).

Structure and shapes on the basis of VBT:



e.g., IF_7 (It is probably the only known example of a non-transition element using three d -orbitals for bonding.)

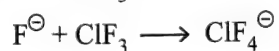
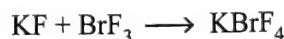
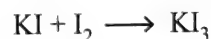
Structure and shapes on the basis of VSEPR theory:

Mole- cule	Total number of electron pairs on A	Bond pairs	Lone pairs	Geometry (shape)
AX	$\frac{7 + (1 \times 1)}{2} = 4$	1	3	Tetrahedral (Linear) 
AX ₃	$\frac{7 + (1 \times 3)}{2} = 5$	3	2	Bent T-shape 
AX ₅	$\frac{7 + (1 \times 5)}{2} = 6$	5	1	Octahedral (square pyramidal) 
AX ₇	$\frac{7 + (1 \times 6)}{2} = 7$	7	0	Pentagonal bipyramidal 

4.18 POLYHALIDE IONS

Ions like I_3^{\ominus} , IBr_2^{\ominus} , $IBrF^{\ominus}$, ClF_4^{\ominus} , etc. which contain more than two, same or different halogen atoms are called polyhalide ions and the corresponding compound is called **polyhalide**.

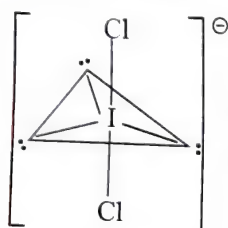
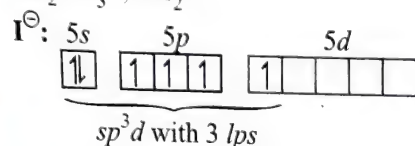
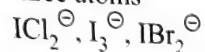
Preparation: Alkali metal halides either in solution or in crystalline salts react with halogens or interhalogen compounds forming ionic polyhalide compounds.



A list of the principle types of polyhalide species which have been characterised are as follows:

Number of halogen atoms in the anion			
3	5	7	9
$\text{Br}_3^\ominus, \text{ClF}_2^\ominus, \text{IBrF}^\ominus$	$\text{ClF}_4^\ominus, \text{ICl}_3\text{F}^\ominus$	$\text{BrF}_6^\ominus, \text{I}_7^\ominus$	I_9^\ominus
$\text{I}_3^\ominus, \text{IBr}_2^\ominus, \text{IBrCl}^\ominus$	BrF_4^\ominus	$\text{IF}_6^\ominus, \text{BrF}_6^\ominus$	BrF_5
ICl_2^\ominus	IF_4^\ominus	ClBr_6^\ominus	—
BrCl_2^\ominus	ICl_4^\ominus	—	—
BrI_2^\ominus	—	—	—
ClBr_2^\ominus	—	—	—

Shape of polyhalide ions: Trihalides or polyhalides containing three atoms

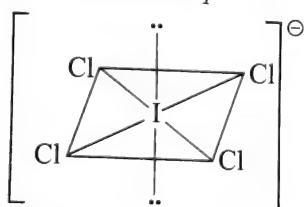
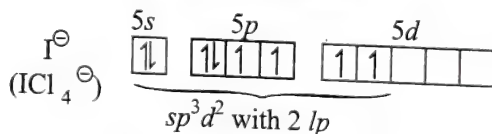


Linear: Bond angle is of the order of $171-179^\circ$

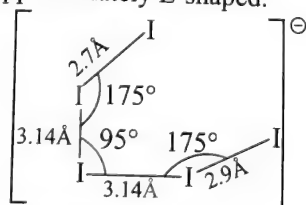
Surprisingly, I_3^\ominus and Br_3^\ominus are slightly unsymmetrical i.e. the two I—I bonds are not equal lengths.

Polyhalides containing five atoms

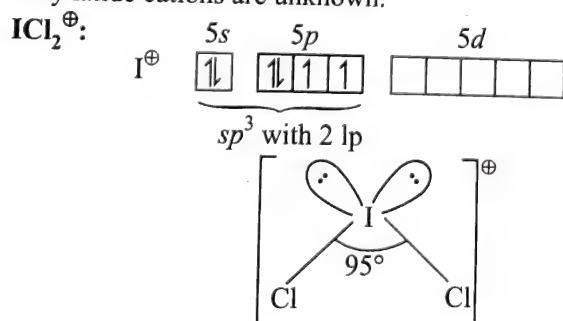
$\text{ICl}_4^\ominus, \text{BrF}_4^\ominus$ are square planar.



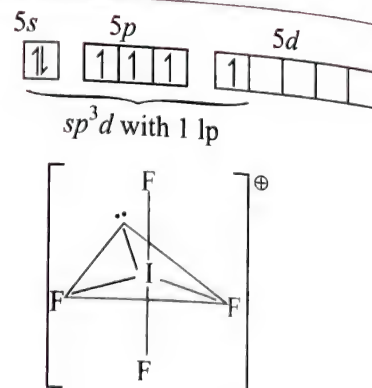
I_5^\ominus in NMe_4I_5 is approximately L-shaped.



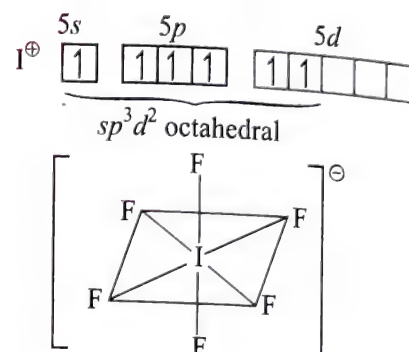
Polyhalide cations are unknown.



IF_4^\oplus :

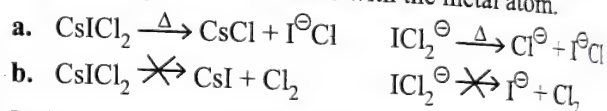


IF_6^\oplus :



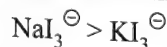
Properties:

1. They are unstable towards thermal dissociation into monohalides and halogen or interhalogen compound. The lighter halogen atom remains with the metal atom.

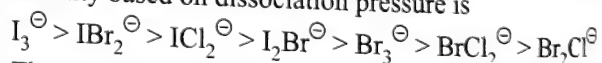


Path (a) is favoured energetically by the high lattice energy of CsCl, i.e., metal halide formed is the one with high lattice energy.

2. Thermal stability of a given type of polyhalide anion increases with the increasing size of the cation.

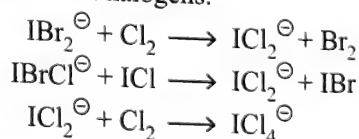


For trihalides formed by same metal, order of thermal stability based on dissociation pressure is

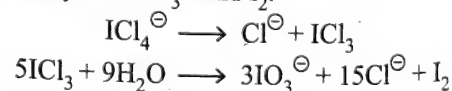
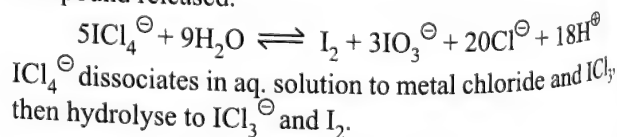


Thermal stability is enhanced, the more symmetrical the polyhalide ion and larger the size of central atom and hence the order.

3. **Reaction with halogens:** The metal polyhalides can often be converted into compounds containing other polyhalides by the action of halogens.



4. **Dissociation in aqueous solution:** The metal polyhalides are unstable in water, leading to a mixture of products which appears to arise from hydrolysis of the interhalogen compound released.



5. Polyhalides dissolve in non-aqueous media, act as halogenating agents, e.g. polybromides have been used in the bromination of β -naphthal, aniline etc.

4.19 PSEUDOHALIDES AND PSEUDOHALOGENS

A few ions are known, consisting of two or more electronegative atoms of which at least one is nitrogen, that have properties similar to those of halide ions. These ions are called pseudohalide ions. Pseudohalide ions are univalent and these form salts resembling halide salts. For example, sodium salts are soluble in water but the silver salts are insoluble. The hydrogen compounds are acids like the halogen acids, HX. The pseudohalide ions are:

Cyanide ion (CN^\ominus);	Iso cyanide ion (NC^\ominus)
Cyanate ion (OCN^\ominus);	Iso cyanate ion (ONC^\ominus)
Thiocyanate ion (SCN^\ominus);	Iso thiocyanate ion (CNC^\ominus)
Selenocyanate ion (SeCN^\ominus);	Tellurocyanate ion (TeCN^\ominus)
Azide ion (N_3^\ominus);	Azido carbon disulphide ion (SCSN_3^\ominus)

The salts formed by above ions are called pseudohalides. As the dimers of halide ions are called halogens, the covalent dimers of the pseudohalide ions are called pseudohalogens or halogenoids. So far only few of pseudohalogens have been isolated and characterised. The pseudohalogens known are:

Cyanogen (CN_2);	Oxycyanogen (OCN_2)
Thiocyanogen (SCN_2);	Selenocyanogen (SeCN_2)
Tellurocyanogen (TeCN_2);	Azido carbon disulphide (SCSN_3)

The best known pseudohalide is CN^\ominus . This resembles Cl^\ominus , Br^\ominus and I^\ominus in the following respects:

- It forms an acid, HCN.
- It can be oxidised to $(\text{CN})_2$ molecule.
- It forms insoluble salts with Ag^\oplus , Pb^{2+} and Hg_2^{2+} .
- It forms large number of complexes similar to halide complexes, e.g., $[\text{Cu}(\text{CN})_4]^{2-}$ and $[\text{CuCl}_4]^{2-}$, $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{CoCl}_6]^{3-}$
- Inter-pseudohalogen compounds ClCN , BrCN and ICN can be formed.
- AgCN is insoluble in water but soluble in ammonia like AgCl .
- HCN is oxidised like HCl.

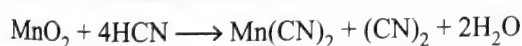
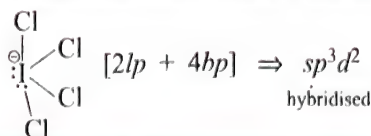
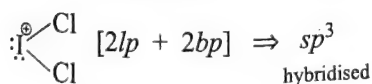
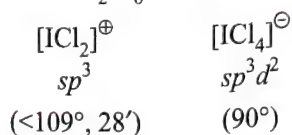


ILLUSTRATION 4.8

Which species of I_2Cl_6 in solid state exist in sp^3 and sp^3d^2 -hybridised state?

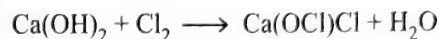
Sol. In solid state I_2Cl_6 exist as:



4.20 BLEACHING POWDER, $\text{CaOCl}_2 \cdot \text{H}_2\text{O}$

Bleaching powder is also called calcium chlorohypochlorite because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid.

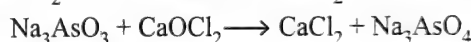
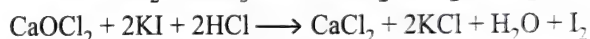
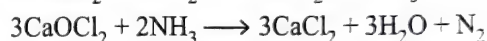
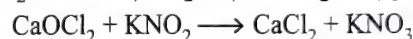
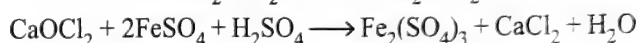
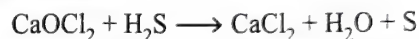
It is manufactured by the action of chlorine on dry slaked lime, $\text{Ca}(\text{OH})_2$, at 40°C.



Properties:

- It is a pale yellow powder. It has a strong smell of chlorine. It is soluble in water but a clear solution is never formed due to the presence of impurities. On account of the formation of nascent oxygen, it shows oxidising and bleaching properties.

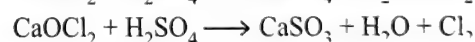
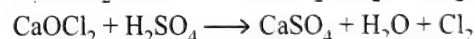
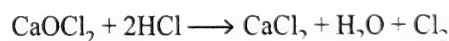
b. Oxidising properties:



c. Bleaching action:

Coloured matter + $[\text{O}] \longrightarrow$ Colourless product

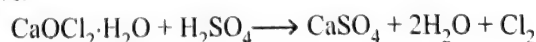
- It loses its chlorine by the action of dilute acids (in excess) or carbon dioxide.



The amount of chlorine obtained from a sample of bleaching powder by treatment with excess of dilute acids or carbon dioxide is called available chlorine. A good sample of bleaching powder contains 35–38% of available chlorine.

Uses: It is used (i) as a disinfectant and germicide especially in the sterilisation of drinking water, (ii) for manufacture of chloroform, (iii) for making wool unshrinkable, (iv) as an oxidising agent in industry and (v) mainly as bleaching agent for cotton, linen and wood pulp. However, delicate articles like straw, silk, ivory, etc., are not bleached by bleaching powder.

Estimation of available chlorine: The maximum percentage of available chlorine as calculated from **Odling's formula** comes to 49%.



M. mass = 145

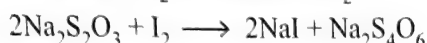
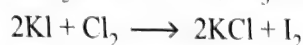
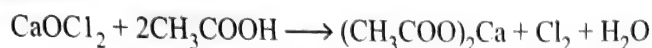
71

145 g of bleaching powder contains 71 g chlorine

100 g of bleaching powder contains $71/145 \times 100 = 49$ g chlorine

The estimation of available chlorine in a given sample of bleaching powder is done volumetrically by the following method.

Iodometric method: A weighed quantity of bleaching powder is suspended in water and treated with excess of acetic acid and potassium iodide. The liberated iodine is estimated by treating with a standard solution of sodium thiosulphate using starch as an indicator.



Let V mL of N/x $\text{Na}_2\text{S}_2\text{O}_3$ be used for W g of a sample of bleaching powder.

V mL of N/x $\text{Na}_2\text{S}_2\text{O}_3$ and V mL of N/x Iodine

$$= V \text{ mL } N/x \text{ Chlorine} = \frac{35.5}{x} \times \frac{V}{1000} \text{ g Chlorine}$$

Thus, % of available chlorine

$$= \frac{35.5 \times V \times 100}{x \times 1000 \times W} = \frac{35.5 \times V}{x \times W}$$

The percentage of available chlorine in the commercial samples of bleaching powder is usually between 33% and 38%. The low value is due to the following factors:

- Incomplete reaction between slaked lime and chlorine during its formation.
- Impurities present in the original slaked lime used for the manufacture.
- Decomposition of bleaching powder when kept in air.

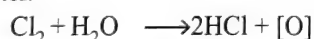
ILLUSTRATION 4.9

Explain the following:

- Dry chlorine does not bleach clothes.
- Fluorine does not form F_3^\ominus (polyhalide) ion.
- HF is least volatile and HCl is most volatile amongst hydrogen halides.

Sol.

- Chlorine acts as a bleaching agent only in the presence of moisture or water, due to liberation of nascent oxygen from water.



Hence dry chlorine cannot bleach clothes.

- Fluorine due to absence of d -orbitals in its valence shell cannot expand its coordination number beyond one. Hence F_3^\ominus ion is not known.
- In covalent compounds, the boiling point increases with increase of molecular mass, as van der Waals forces increases. The volatility, thus decreases in covalent compounds with increase in molecular mass. However, hydrogen bonding is present in HF. Due to which, the boiling point of HF is higher and the volatility is less. Thus the volatility of hydrogen halides can be represented as

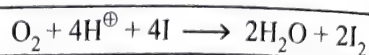
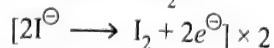
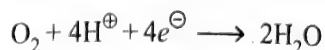
Volatility: $\text{HCl} > \text{HBr} > \text{HI} > \text{HF}$

ILLUSTRATION 4.10

- Pure HI kept in a bottle acquires a brown colour after sometime. Why?
- Ferric iodide is very unstable but ferric chloride is stable. Why?
- KHF_2 is well known but KClO_2 and KBrO_2 do not exist. Why?

Sol.

- HI is a strong reducing agent. It is oxidised by oxygen of the air, i.e. aerial oxidation of HI occurs.



The iodine liberated gives a brown colour to the solution.

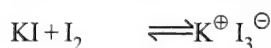
- Iodide ion is a strong reducing agent and reduces ferric ions into ferrous ions, hence ferric iodide is unstable. On the other hand, chloride ion is a weak reducing agent and does not reduce ferric to ferrous ion and thus ferric chloride is stable.
- Hydrofluoric acid exists as dimeric molecule (H_2F_2) due to hydrogen bonding. HF thus exhibits dibasic nature and forms two series of salts, KHF_2 (as K^\oplus and F^\ominus H-F) and KF (K^\oplus and F^\ominus). HCl and HBr exist as monomeric molecules as hydrogen bonding is not present.

ILLUSTRATION 4.11

- Iodine dissolves more in KI solution than in water. Why?
- Colour of KI solution containing starch turns deep blue when chlorine water is added. Explain.

Sol.

- Iodine, I_2 is a covalent molecule. Hence it is less soluble in polar solvent, i.e. water, H_2O . In KI solution, KI reacts with water to form KI_3 which is an ionic compound. $\text{K}^\oplus \text{I}_3^\ominus$. Being ionic, KI_3 is more soluble in water.



- Chlorine being a strong oxidising agent displaces iodine from KI i.e., oxidises I^\ominus to I_2 . Iodine is absorbed by starch and thus deep blue coloured solution is obtained due to formation of starch- I_2 adsorption complex.

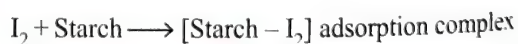
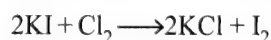


ILLUSTRATION 4.12

Mention the conditions in which the following statements are correct.

- Chlorine is a good bleaching agent.
- A mixture of H_2 and Cl_2 explodes.
- Cl_2 reacts with NaOH solution to produce sodium chloride and sodium hypochlorite (along with water).
- Cl_2 reacts with NaOH solution to produce sodium chloride and sodium chlorate (along with water).
- Cl_2 substitutes hydrogen atoms of a molecule of methane.
- Cl_2 reacts with ammonia to form nitrogen and ammonium chloride.
- Cl_2 reacts with lime to form bleaching powder.
- Iodine dissolves freely in water.
- Chlorine forms an addition product with SO_2 .

- Sol.**
- In presence of moisture, chlorine acts as a good bleaching agent.
 - A mixture of H_2 and Cl_2 explodes on exposure to direct sunlight.
 - Cl_2 reacts with NaOH solution to produce NaCl, sodium hypochlorite and H_2O in cold and dilute conditions.
 - When NaOH solution is hot and concentrated, it reacts with Cl_2 to produce sodium chloride, sodium chlorate and water.
 - In diffused sunlight, Cl_2 substitutes hydrogen atoms of a molecule of methane.
 - When NH_3 is in excess, it reacts with Cl_2 to form N_2 and NH_4Cl .
 - On passing Cl_2 over dry slaked lime, bleaching powder is formed.
 - Iodine dissolves freely in water in presence of KI.
 - In dry conditions, Cl_2 forms an addition product with SO_2 .

CONCEPT APPLICATION EXERCISE 4.1

- Bond dissociation energy of F_2 is less than that of Cl_2 . Give reason.
- Why fluorine does not exhibit any positive oxidation state?
- Bleaching of flowers by chlorine is permanent, while that by sulphur dioxide is temporary. Explain.
- Arrange $HOCl$, $HClO_2$, $HClO_3$ and $HClO_4$ in order of (i) acidic strength and (ii) oxidising power. Give reason.
- The negative value of electron gain enthalpy is less for fluorine than for chlorine. Why?
- Despite the fact that fluorine is more electronegative than iodine, yet HF is less acidic as compared to HI . Explain.
- What happens when Cl_2 is passed through a hot concentrated solution of a base like $Ba(OH)_2$?
- Why fluorine never acts as the central atom in polyatomic interhalogen compounds?
- ClF_3 exists but FCl_3 does not. Why?
- Addition of Cl_2 to KI solution gives it a brown colour but excess of Cl_2 turns it colourless. Why?
- Give relevant chemical equations for the preparation of:
 - Chlorine from sodium chloride.
 - Iodine from Kelp.
 - Hydrobromic acid from potassium bromide.
 - Bleaching powder from slaked lime.
 - $KClO_3$ from sodium chloride.
- A sodium salt (A) is heated with conc. sulphuric acid. The evolved gas turns moist litmus paper red and produces white fumes in contact with a glass rod moistened with ammonia solution. It also gives white precipitate when passed through $AgNO_3$ solution. When the salt is heated with MnO_2 and conc. H_2SO_4 , a gas with an irritating smell is evolved which turns starch-iodide paper blue. Identify the salt and the gaseous product evolved from it. Explain your answer with relevant chemical equations.
- A certain compound (X) shows the following reactions.
 - When KI is added to an aqueous suspension of (X) containing acetic acid, iodine is liberated.
 - When CO_2 is passed through an aqueous suspension of (X), the turbidity transforms to a precipitate.
 - When the paste of (X) in water is heated with ethyl alcohol, a product of anaesthetic use is obtained. Identify (X) and write down chemical equations for reactions at steps (a), (b) and (c).
- A colourless inorganic compound (A) imparts a green colour to flame. Its solution does not give any precipitate with H_2S . Its solution gives white precipitate with conc. H_2SO_4 which is insoluble in dil. H_2SO_4 . When it is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 , a red gas is evolved. The gas when passed through aqueous NaOH solution turns it yellow. Identify the compound (A) and give chemical reactions.
- Give balanced chemical reactions for the following:
 - Sodium iodate is treated with sodium bisulphite solution.
 - Chlorine is passed through hot NaOH solution.
 - Chlorine is passed through aqueous potassium hydroxide.
 - Chlorine gas is bubbled through a solution of ferrous bromide.
 - Iodine reacts with conc. HNO_3 .
 - Chlorine is passed over slaked lime.
 - Sodium chloride is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 .
 - Potassium iodide is heated with MnO_2 and conc. H_2SO_4 .
 - Chlorine reacts with Na_2SO_3 solution.
 - Iodine is added to stannous chloride solution.
 - Chlorine is passed through a suspension of iodine.
 - Cl_2 is passed through a suspension of $CaCO_3$.
 - Chlorine gas is passed through dry and aqueous sulphur dioxide.
 - Bromine reacts with Na_2CO_3 solution.
 - Potassium iodide is added to bleaching powder containing dilute acetic acid.
- Pseudohalogens or halogenides are complex molecules which behaves like halogens. Among the following list CN^\ominus (cyanide), OCN^\ominus (cyanate), SCN^\ominus (thio-cyanate), $SeCN^\ominus$ (selenocyanate), $TeCN^\ominus$ (tellurocyanate), ONC^\ominus (isocyanate), N_3^\ominus (azide), cyanogen $(CN)_2$, oxycyanogen $(OCN)_2$, thiocyanogen $(SCN)_2$, tellurocyanogen $(TeCN)_2$, azidecarbon disulphide $(SCS N_3)$, $ClCN$, $BrCN$, ICN , ICl , IF_7 , IF_5 , I_3^\ominus , ICl_2^\ominus , I^\ominus , I^\oplus , I_3^\oplus .
 - Which are inter pseudohalogens?
 - Which are interhalogens or their anions?
 - Which are polyhalides?
 - Which are neither (a), (b), (c) or pseudohalogen or their anions?
 - Which are pseudohalogens or their anions?

17. When carnalite is crystallised, the mother liquor contains a more water soluble salt (X) which gives pink mass in cobalt nitrate test when (X) is heated with conc. H_2SO_4 brown gas is evolved. (X) gives, with AgNO_3 solution, a pale yellow (Cream. Coloured) ppt. slightly soluble in NH_4OH . Identify (X).

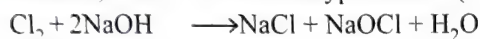
Solved Examples

EXAMPLE 4.1

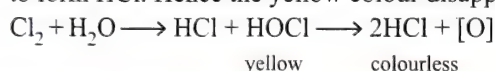
- What happens when Cl_2 reacts with cold dilute solution of sodium hydroxide?
- Why does chlorine water lose its yellow colour on standing?

Sol.

- With cold dilute solution of sodium hydroxide, Cl_2 undergoes disproportionation to give a mixture of sodium chloride, NaCl and sodium hypochlorite (NaOCl).



- Chlorine water is yellow due to the presence of hypochlorous acid, HOCl . On standing, HOCl being unstable decomposes to form HCl . Hence the yellow colour disappears.

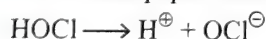


EXAMPLE 4.2

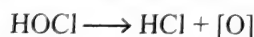
- When a moist blue litmus paper is dipped in a solution of hypochlorous acid, it first turns red and then latter gets decolourised. Explain.
- Iodine is liberated when KI is added to a solution of Cu^{2+} ions but Cl_2 is not liberated when KCl is added to a solution of Cu^{2+} ions. Why?

Sol.

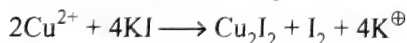
- Hypochlorous acid, HOCl behaves as an acid and hence blue litmus paper turns red.



Hypochlorous acid also acts as a bleaching agent and thus decolourises red litmus by the nascent oxygen.



- The iodide ion (I^-) being a strong reducing agent, reduces Cu^{2+} to Cu^+ and itself gets oxidised to I_2 .



Since Cl^- ion does not act as a reducing agent, therefore, Cl_2 is not liberated when KCl is added to a solution of Cu^{2+} ions.

EXAMPLE 4.3

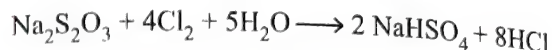
$\text{Na}_2\text{S}_2\text{O}_3$ reacts with Cl_2 and I_2 to give different oxidation products. Give the equations involved and a plausible explanation of their contrasting behaviour.

Sol. Cl_2 is a stronger oxidising agent than I_2 and hence oxidises $\text{Na}_2\text{S}_2\text{O}_3$ to NaHSO_4 in which the oxidation state of S increases

from +2 to +6, while with only I_2 solution, sodium tetrathionate, $\text{Na}_2\text{S}_4\text{O}_6$ is obtained in which the oxidation state of S increases from +2 to +2.5 only.

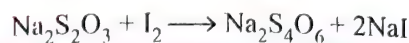
(+2)

(+6)



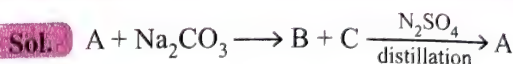
(+2)

(+2.5)

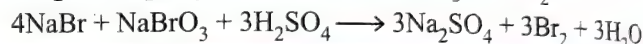


EXAMPLE 4.4

A liquid 'A' is treated with Na_2CO_3 solution. A mixture of two salts 'B' and 'C' is produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid 'A' again. Identify 'A', 'B' and 'C' and write the equations involved.



Liquid 'A' is bromine, which on treatment with Na_2CO_3 forms a mixture of NaBr and NaBrO_3 . The mixture on acidification and distillation gives liquid bromine again.



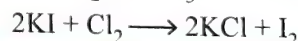
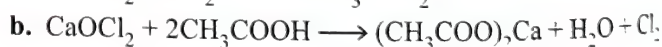
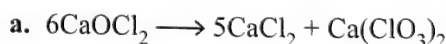
EXAMPLE 4.5

An inorganic compound (X) gives a brick red flame on performing flame test. This compound gives the following tests also.

- Smells of chlorine when placed in moist air.
- If KI and CH_3COOH are added to the suspension in water, a brown colour is obtained.

Identify (X) and write down equations for reactions at steps (a) and (b).

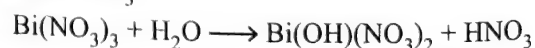
Sol. Compound (X) gives a brick red flame in flame test. Thus, it is a calcium compound. The smell of chlorine on exposure suggests that it is a bleaching powder. It is confirmed by reaction (b).



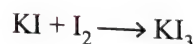
EXAMPLE 4.6

Gradual addition of KI solution to $\text{Bi}(\text{NO}_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions.

Sol. $\text{Bi}(\text{NO}_3)_3$ undergoes hydrolysis to produce nitric acid. HNO_3 oxidises KI , i.e., I_2 (brown ppt.) is formed. The precipitated iodine dissolves in excess of KI and forms a yellow coloured solution of KI_3 .



Brown ppt.

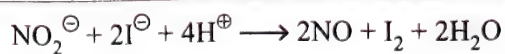


Yellow soln.

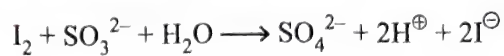
EXAMPLE 4.7

Give reason: The brown colour of an acidified dilute solution of iodine in aqueous potassium iodide is intensified by addition of sulphite.

Sol. Nitrite ion being stronger oxidising agent than iodide ion, oxidises $I^- \rightarrow I_2$ and itself gets reduced to NO. Thus the brown colour is intensified.



Whereas sulphite is weaker oxidising agent than iodide and hence I_2 is reduced to I^- and the solution becomes colourless or the brown colour is discharged.



Exercises

Single Correct Answer Type

Physical and Chemical Properties of Halogens

- Bond energy of halogens are
 - (1) $F_2 > Cl_2 > Br_2 > I_2$
 - (2) $Cl_2 > Br_2 > F_2 > I_2$
 - (3) $Cl_2 > F_2 > Br_2 > I_2$
 - (4) $Br_2 > Cl_2 > F_2 > I_2$
- IE of halogens are
 - (1) $F > Cl > Br > I$
 - (2) $Cl > F > Br > I$
 - (3) $Cl > Br > I > F$
 - (4) $Cl > Br > F > I$
- Which of the following does not liberate Br_2 from KBr ?
 - (1) I_2
 - (2) Cl_2
 - (3) conc. H_2SO_4
 - (4) F_2
- Which has the highest degree of hydrogen bonding?
 - (1) HCl
 - (2) H_2O
 - (3) HF
 - (4) HBr
- In case of halogens strong oxidising character is favoured by their
 - (1) Low dissociation energy
 - (2) Low E.A.
 - (3) Low IE
 - (4) Low hydration energy of X^\ominus ion
- Cl_2 is
 - (1) More reactive than F_2
 - (2) Less reactive than Br_2
 - (3) More reactive than Br_2 and I_2
 - (4) Less reactive than I_2
- The sum of energy term involved in the reaction:

$$\frac{1}{2} X_{2(g)} \longrightarrow X^\ominus_{(aq)}$$
 is highest in case of
 - (1) Fluorine
 - (2) Chlorine
 - (3) Bromine
 - (4) Iodine
- Which one of the following oxidises water to oxygen with large evolution of heat?
 - (1) Chlorine
 - (2) Bromine
 - (3) Iodine
 - (4) Fluorine
- Which one of the following halogen acids has the lowest melting point?
 - (1) HF
 - (2) HCl
 - (3) HBr
 - (4) HI
- Which of the following halogen acids has the highest boiling point?
 - (1) HF
 - (2) HCl
 - (3) HBr
 - (4) HI
- Size of the iodine species follows the order:
 - (1) $I^\oplus > I^\ominus > I$
 - (2) $I > I^\oplus > I^\ominus$
 - (3) $I > I^\ominus > I^\oplus$
 - (4) $I^\ominus > I > I^\oplus$
- Volatile nature of halogens is because
 - (1) The halogen molecules are more reactive
 - (2) The force existing between the molecules are only weak van der Waal forces
 - (3) Halogen molecules are bounded by strong forces
 - (4) Halogen molecules are bounded by electrostatic forces.
- Which of the following will displace the halogen from the solution of the halide?
 - (1) Br_2 added to $NaCl$ solution
 - (2) Cl_2 added to KCl solution
 - (3) Cl_2 added to NaF solution
 - (4) Br_2 added to KI solution
- Which one of the following is the most basic?
 - (1) I
 - (2) Br
 - (3) Cl
 - (4) F
- On heating NaX with H_2SO_4 and MnO_2 the halogens that cannot be prepared is _____.
 - (1) I_2
 - (2) Cl_2
 - (3) Br_2
 - (4) F_2
- In the reaction:

$$3Br_2 + 6OH^\ominus \longrightarrow 5Br^\ominus + BrO_3^\ominus + 3H_2O$$
 Br_2 is
 - (1) Oxidised
 - (2) Reduced
 - (3) Disintegrated
 - (4) Disproportionated
- Tincture of iodine contains
 - (1) I_2 , KI and C_2H_5OH
 - (2) I_2 and C_2H_5OH
 - (3) KI and C_2H_5OH
 - (4) I_2 and H_2O
- In the reaction $I_2 + 2OH^\ominus \longrightarrow I^\ominus + IO^\ominus + H_2O$
 I_2 is
 - (1) Oxidised
 - (2) Reduced
 - (3) Oxidised and reduced
 - (4) Forms complex
- Estimation of reducing substances by the use of standard I_2 .

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^\ominus$$
 is called
 - (1) Iodimetry
 - (2) Iodometry
 - (3) Oxidising
 - (4) Reducing
- Estimation of oxidising substance involving the liberation of I_2 and subsequent volumetric estimation of I_2 are referred to as

$$2Cu^{2+} + 4I^\ominus \longrightarrow Cu_2I_2 + I_2$$

$$I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^\ominus$$
 - (1) Iodimetry
 - (2) Iodometry
 - (3) Oxidising
 - (4) Reducing
- On passing Cl_2 water in a mixture of KBr and KI solution in contact with CCl_4 continuously with occasional shaking, we observe
 - (1) Orange CCl_4 layer changing to violet
 - (2) Persisting violet CCl_4 layer
 - (3) Persisting brown layer
 - (4) Violet layer changing into brown and finally colourless
- When chlorine water is added to an aqueous solution of sodium iodide in the presence of chloroform, a violet

- colouration is obtained. On adding more of chlorine water and vigorous shaking, the violet colour disappears. This shows the conversion of into
- (1) I_2 , HIO_3 (2) I_2 , HI
 (3) HI , HiO_3 (4) I_2 , HOI
23. The products of the chemical reaction between $Na_2S_2O_3$, Cl_2 and H_2O are
 (1) S , HCl , Na_2SO_4 (2) S , HCl , Na_2S
 (3) S , HCl , Na_2SO_3 (4) S , $NaClO_3$
24. Fluorine on reaction with $KIO_3(aq.)$ gives (A) and on reaction with $KHSO_4$ gives (B). (A) and (B) are
 (1) KIO_4 , $K_2S_2O_3$ (2) KI , F_2O
 (3) HF , $K_2S_2O_8$ (4) I_2 , $K_2S_2O_8$
25. $Br_2 + OH^- \xrightarrow{HOT} (A) + (B)$
 (A) + (B) + $H^+ \longrightarrow Br_2$
 (A) gives yellow precipitate with $AgNO_3$. (A) and (B) are
 (1) Br^- , BrO^- (2) Br^- , BrO_3^-
 (3) BrO^- , BrO_3^- (4) BrO^- , BrO_4^-
26. Which one of the following represents the reaction between fluorine and cold $NaOH$ (dil.)?
 (1) $2F_2 + 4NaOH \longrightarrow 4NaF + 2H_2O + O_2$
 (2) $3F_2 + 6NaOH \longrightarrow 5NaF + NaFO_3 + 3H_2O$
 (3) $F_2 + 2NaOH \longrightarrow NaF + NaOF + H_2O$
 (4) $2F_2 + 2NaOH \longrightarrow 2NaF + OF_2 + H_2O$
27. Which one of the following pairs of reactants does not form oxygen when they react with each other?
 (1) F_2 , $NaOH$ solution (hot, conc.)
 (2) F_2 , H_2O
 (3) Cl_2 , $NaOH$ solution (cold, dilute)
 (4) $CaOCl_2$, H_2SO_4 (dilute, small amount)
28. One atom of _____ combines with one atom of bromine.
 (1) Ar (2) Rb
 (3) Mg (4) HCl
29. The colour of I_2 is violet because it
 (1) Absorbs violet light
 (2) Does not absorb light
 (3) Absorbs yellow and green light
 (4) None of the above
30. The boiling points of halogens increase with increase in molecular weight, it is because
 (1) As the size increases molecules undergo association leading to higher stability
 (2) Bond strength increases due to increase in electronegativity
 (3) van der Waals forces increase with increase in number of electrons per mole
 (4) None of the above
31. The catalyst used in the Deacon's process for the manufacture of chlorine is
 (1) Cu (2) An alloy of copper
 (3) $CuCl_2$ (4) CuS
32. Bromine occurs as a bromide in a mineral called
 (1) Nitre (2) Tincal
 (3) Common salt (4) Carnallite
33. The halide which does not give a precipitate with $AgNO_3$ is
 (1) F^- (2) Cl^-
 (3) Br^- (4) I^-
34. Which halogen can be purified by sublimation?
 (1) F_2 (2) Cl_2
 (3) Br_2 (4) I_2
35. The halogen having the smallest covalent radius is
 (1) I (2) Cl
 (3) Br (4) F
36. The strongest oxidising agent among the following is
 (1) Ozone (2) Oxygen
 (3) Fluorine (4) Chlorine
37. A 500 g toothpaste sample has 0.2 g fluoride concentration. What is the concentration of F^- in ppm?
 (1) 250 (2) 200
 (3) 400 (4) 1000
38. The interatomic distances in H_2 and Cl_2 molecules are 74 and 198 pm respectively. The bond length of HCl is
 (1) 272 pm (2) 136 pm
 (3) 124 pm (4) 248 pm
39. In the halogen group, chlorine is a gas, bromine is a liquid and iodine exists as solid crystals. Then the next halogen astatine (At) would be
 (1) Solid at room temperature
 (2) Having higher electronegativity
 (3) Liquid with higher ionisation enthalpy
 (4) Least atomic size
40. Iodine is placed between two liquids C_6H_6 and water:
 (1) It dissolves more in C_6H_6
 (2) It dissolves more in water
 (3) It dissolves equally in both
 (4) Does not dissolve in both
41. Mixture of I_2 and sand can be separated by:
 (1) Dissolving in water and filtering
 (2) Fractional crystallisation
 (3) Sublimation
 (4) None of the above
42. Which one is the strongest bond?
 (1) $Cl-F$ (2) $F-F$
 (3) $Br-F$ (4) $Br-Cl$
43. Which of the following trend correctly represents the stability of oxides of halogens.
 (1) $I > Cl > Br$ (2) $Cl > I > Br$
 (3) $Br > Cl > I$ (4) $Br > I > Cl$
44. Which is/are true statement(s)?
 (1) The ionic character of $M-X$ bond decreases in the order $M-F > M-Cl > M-Br > M-I$
 (2) HI is strongest acid of HF , HCl , HBr and HI

(3) Basic nature of X^\ominus is in order $F^\ominus > Cl^\ominus > Br^\ominus > I^\ominus$

(4) All the above are correct statements

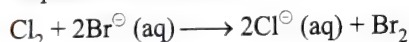
45. The three elements X, Y and Z with electronic configurations shown below all form hydrides:

Element	Electronic configuration
X	$1s^2 2s^2 2p^2$
Y	$1s^2 2s^2 2p^6 3s^1$
Z	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$

Which set of properties match correctly with properties of the hydrides of these elements:

	Hydride of X	Hydride of Y	Hydride Z
(1)	Colourless gas insoluble in H_2O	Silver/grey solid reacts with H_2O to form an alkaline solution.	Colourless gas forms a strong acid in H_2O
(2)	Non-polar compound reacts with Cl_2 in light	Silver/grey ionic solid with formula YH_2	Forms when water is added to phosphorus and elements Z.
(3)	Colourless gas which burns with air	Silver/grey solid which reacts violently with acids	Colourless, corrosive liquid at STP
(4)	Colourless liquid, no reaction with H_2O	Silver/grey solid forms H_2 and H_2O	Ionic solid with formula ZH

46. Bromine is commercially prepared from sea water by displacement reaction



Br_2 gas thus formed is dissolved into solution of Na_2CO_3 and then pure Br_2 is obtained by treatment of the solution with:

- (1) HI (2) H_2SO_4
(3) NaOH (4) $Ca(OH)_2$
47. Which of the following properties of halogens increase with increasing atomic number?

- (I) Ionization energy
(II) Ionic radius
(III) Bond energy of the X_2 molecule
(IV) Enthalpy of vaporization
- (1) I, II, III (2) I, III
(3) II, IV (4) IV

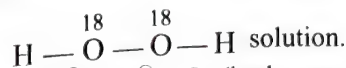
48. The high oxidizing power of fluorine is due to

- (1) High heat of dissociation and high heat of hydration
(2) Low heat of dissociation and high heat of hydration
(3) High heat of dissociation and low heat of hydration
(4) High electron affinity

49. Affinity for hydrogen decreases in the group fluorine to iodine. Which of the halogen acids should have highest dissociation enthalpy?

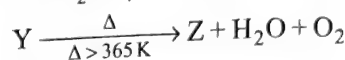
- (1) HF (2) HCl
(3) HBr (4) HI

50. Predict the correct product when Cl_2 passed through



- (1) $H^\oplus + Cl^\ominus + O_2$ (both oxygen having 18)
(2) HOCl and $HClO_2$ (all oxygen having 18)
(3) $HClO_4$ and HCl (all oxygen having 18)
(4) Cl_2O and H_2O (all oxygen having 18)

51. $Cl_2(g) + Ba(OH)_2 \longrightarrow X(aq.) + BaCl_2 + H_2O$



Y and Z are respectively:

- (1) $HClO_4$, Cl_2O_7 (2) $HClO_3$, ClO_2
(3) $HClO_3$, ClO_6 (4) $HClO_4$, ClO_2

52. Cryolite and Caliche are the source of halogens A and B respectively. A and B are

- (1) Fluorine, Bromine (2) Sodium, Iodine
(3) Fluorine, Iodine (4) Sodium, Bromine

53. Which of the following statements are correct for all three halogens (X), Cl, Br and I?

- (1) They all form strong acid of the type HX
(2) They all need to gain one electron to acquire stable configuration
(3) Both (1) and (2) are correct
(4) None of the above is correct

Compounds of Halogens

54. The oxidising ability of perhalates are in the order:

- (1) $ClO_4^\ominus > BrO_4^\ominus > IO_4^\ominus$ (2) $ClO_4^\ominus < BrO_4^\ominus < IO_4^\ominus$
(3) $BrO_4^\ominus > IO_4^\ominus > ClO_4^\ominus$ (4) $IO_4^\ominus < BrO_4^\ominus < ClO_4^\ominus$

55. Acid strength is in the order:

- (1) $HClO_4 > HIO_4 > HBrO_4$ (2) $HClO_4 > HBrO_4 > HIO_4$
(3) $HClO_4 < HBrO_4 > HIO_4$ (4) None

56. Oxidising power of halogens are

- (1) $F_2 > Cl_2 > Br_2 > I_2 > At_2$ (2) $At_2 > F_2 > Br_2 > Cl_2 > F_2$
(3) $Cl_2 > Br_2 > F_2 > I_2 > At_2$ (4) $Cl_2 > F_2 > Br_2 > I_2 > At_2$

57. Relative strength of acids are

- (1) $HF < HCl < HBr < HI$ (2) $HF > HCl > HBr > HI$
(3) $HCl < HF < HBr < HI$ (4) $HI < HBr < HF < HI$

58. Bond strength of halogen acids are

- (1) $HF > HCl > HBr > HI$ (2) $HCl > HF > HBr > HI$
(3) $HCl > HBr > HF > HI$ (4) $HI > HBr > HCl < HF$

59. Reducing properties of halogen acids are

- (1) $HF > HCl > HBr > HI$ (2) $HF < HCl < HBr < HI$
(3) $HCl > HF > HBr > HI$ (4) $HCl > HBr > HF < HI$

60. Which of the following halogen acid is a liquid?

- (1) HF (2) HCl
(3) HBr (4) HI

61. Which of the following exists as an associated molecule even in the vapour state?

- (1) HCl (2) HBr
(3) HF (4) HI

62. The relative acidic strength, stability and oxidising agent of oxy-acids of chlorine are

- (1) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$
 (2) $\text{HClO}_4 > \text{HClO}_2 > \text{HClO}_3 > \text{HOCl}$
 (3) $\text{HOCl} < \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$
 (4) $\text{HClO}_3 > \text{HClO}_2 > \text{HClO}_4 > \text{HOCl}$

63. In gaseous state, ionic character is greatest in

- (1) HBr (2) HF
 (3) HCl (4) HI

64. Mark the strongest reducing agent.

- (1) H_2F_2 (2) HCl
 (3) HBr (4) HI

65. HCl and HF are prepared by heating their salt (NaCl and CaF_2) with conc. H_2SO_4 but HI and HBr cannot be prepared by similar reaction because HBr and HI have

- (1) Reducing properties (2) Oxidising property
 (3) Complex forming ability (4) None of these

66. HBr and HI may be obtained by heating bromide and iodine with syrupy phosphoric acid not with H_2SO_4 because H_2SO_4 is

- (1) A weaker acid (2) Less stable
 (3) An oxidising agent (4) A reducing agent

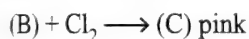
67. Which of the following is soluble in water?

- (1) AgF (2) AgBr
 (3) AgCl (4) AgI

68. A greenish yellow gas reacts with an alkali metal hydroxide to form a halate which can be used in fireworks and safety matches. The gas and the halate are

- (1) Br_2 , KBrO_3 (2) Cl_2 , KClO_3
 (3) I_2 , NaIO_3 (4) I_2 , KIO_3

69. For $(\text{A}) + \text{K}_2\text{CrO}_3 + \text{air} \xrightarrow{\text{Heat}} (\text{B})$



Which of the following is correct?

- (1) (A) is black, MnO_2 ; (B) is blue, K_2MnO_4 and (C) is pink, KMnO_4
 (2) (A) is green, Cr_2O_3 ; (B) is yellow, K_2CrO_4 and (C) is pink, $\text{K}_2\text{Cr}_2\text{O}_7$
 (3) (A) is black, MnO_2 ; (B) is green, K_2MnO_4 and (C) is pink, KMnO_4
 (4) (A) is black, Bi_2O_3 ; (B) is colourless, KBiO_2 and (C) is pink, KBiO_3

70. Euchlorine is

- (1) Obtained by heating perchlorate with conc. HCl
 (2) A chloride of europium
 (3) A mixture of Cl_2 and Cl_2O_7
 (4) A mixture of Cl_2 and ClO_2

71. Which is incorrectly matched?

- (1) $\text{CsBr}_3 \rightleftharpoons \text{Cs}^\oplus + \text{Br}_3^\ominus \rightleftharpoons \text{Cs}^\oplus + \text{Br}^\ominus + \text{Br}_2$
 (2) $\text{I}_4\text{O}_9 \rightleftharpoons \text{I}^{3+} + 3(\text{IO}_3)^\ominus$
 (3) $\text{AgBrO}_3 \rightleftharpoons \text{Ag}^\oplus \text{Br}_3^\ominus$
 (4) $\text{I}_2\text{O}_4 \rightleftharpoons \text{IO}_2^\oplus + \text{IO}_2^\ominus$

72. A certain compound (X) when treated with copper sulphate solution yields a brown precipitate. On adding hypo solution the precipitate turns white. The compound is

- (1) K_2CrO_3 (2) KI
 (3) KBr (4) K_3PO_4

73. KClO_3 on reaction with SO_2 gives (A) and on reaction with conc. H_2SO_4 gives (B). (A) and (B) are

- (1) KCl, HClO_4 (2) Cl_2 , ClO_2
 (3) KCl, HClO_3 (4) Cl_2 , HClO_4

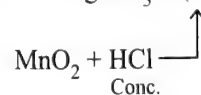
74. 10 g of bleaching powder on reaction with KI required 50 mL of 2N hypo solution. Thus, % of bleaching powder is

- (1) 100 (2) 80
 (3) 63.5 (4) 35.5

75. $\text{HClO}_4 + \text{P}_2\text{O}_5 \longrightarrow (\text{A}) + (\text{B})$

- (A) and (B) are
 (1) HClO_3 , H_3PO_4 (2) Cl_2O_6 , HPO_3
 (3) ClO_2 , H_3PO_4 (4) Cl_2O_7 , HPO_3

76. $\text{AgClO}_3 + (\text{A}) \longrightarrow (\text{B}) + (\text{C}) + (\text{D})$



The substances (A), (B), (C) and (D) are

- (1) Cl_2 , AgCl , ClO_2 , O_2 (2) Cl_2 , Ag, Cl_2O_6 , O_2
 (3) H_2 , AgCl , H_2O , O_2 (4) HClO , AgCl , ClO_2 , O_2

77. Select the correct statement(s):

- (1) Cl_2O and ClO_2 are used as bleaching agents and as germicides.
 (2) ClO_2 is the anhydride of HClO_2 and HClO_3 .
 (3) I_2O_5 is used in the quantitative estimation of CO.
 (4) All of the above are correct.

78. Which bond has the greatest polarity?

- (1) H-Cl (2) H-Br
 (3) H-I (4) H-F

79. Bleaching properties of bleaching powder are due to its

- (1) Oxidising properties (2) Reducing properties
 (3) Basic properties (4) Disinfecting properties

80. Bleaching powder is a mixture of

- (1) Calcium hypochlorite and calcium chloride
 (2) Calcium chlorate and calcium chloride
 (3) Calcium hypochlorite and basic calcium chloride
 (4) Calcium chlorate and calcium hydroxide

81. One can draw the map of a building on a glass plate by

- (1) HI (2) HF
 (3) HBr (4) HCl

82. The tetrahedral nature of the three bonds in a chlorate ion (ClO_3^\ominus) is due to

- (1) The presence of a lone pair of electrons
 (2) sp^3 -hybridisation
 (3) sp^2 -hybridisation
 (4) Trigonal bipyramidal shape of ion

83. Which one of the following acts as an antichlor?
 (1) MnO_2 (2) $\text{Na}_2\text{S}_2\text{O}_3$
 (3) $\text{K}_2\text{Cr}_2\text{O}_7$ (4) Na_2SO_4
84. One gas bleaches the colour of flowers by reduction and other by oxidation. These gases are
 (1) SO_2 and Cl_2 (2) CO and Cl_2
 (3) NH_3 and SO_2 (4) H_2S and Br_2
85. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order.
 ClOH(I) BrOH(II) IOH(III)
 (1) $\text{I} > \text{II} > \text{III}$ (2) $\text{II} > \text{I} > \text{III}$
 (3) $\text{III} > \text{II} > \text{I}$ (4) $\text{I} > \text{III} > \text{II}$
86. Which has maximum pH in aqueous solution?
 (1) NaClO (2) NaClO_2
 (3) NaClO_3 (4) NaClO_4
87. A gas X is passed through water to form a saturated solution. The aqueous solution on treatment with AgNO_3 gives a white precipitate. The saturated aqueous solution also dissolves Mg ribbon with evolution of colourless gas Y, X and Y are respectively:
 (1) CO_2, Cl_2 (2) Cl_2, CO_2
 (3) Cl_2, H_2 (4) H_2, Cl_2
88. Which one is the anhydride of HClO_4 ?
 (1) Cl_2O_7 (2) ClO_2
 (3) Cl_2O_6 (4) Cl_2O
89. Which of the following is not the characteristic of inter-halogen compounds?
 (1) They have low boiling points and are highly volatile
 (2) They are covalent in nature
 (3) They are quite unstable but none of them is explosive
 (4) They are more reactive than halogens
90. Consider the oxy acids HClO_n series, here value of n is 1 to 4. Then **incorrect** statement regarding these oxy acids is:
 (1) 'Cl—O' bond order decreases with decreasing value of n .
 (2) Thermal stability of oxy acids decreases with increasing value of n .
 (3) Oxidizing power of oxy acids increases with decreasing value of n .
 (4) Acidic character of oxy acids increases with increasing value of n .
91. In, $\text{Cl}_2\text{O}_6(l) + \text{HF} \longrightarrow \text{P} + \text{Q}$
 If H^+ of acid HF attaches with Q, then correct option for hybridization of Cl-atom and $\angle \text{OCIO}$ in the P and Q ions:
 (1) Q: sp^3 ; $> 109^\circ 28'$ (2) Q: sp^3 ; $109^\circ 28'$
 (3) P: sp^3 ; $< 109^\circ 28'$ (4) P: sp^1 ; $> 120^\circ$
92. The correct statement regarding $\text{ClO}_n^{(n-1)}$ molecular ion is:
 (1) On increasing value of n , hybrid orbitals on central atom increase
 (2) On increasing value of n , oxidation number of central atom increases
 (3) On increasing value of ' n ', 'Cl—O' bond length increases
 (4) On decreasing value of ' n ', 'Cl—O' bond order increases
93. In the preparation of HBr or HI , NaX ($X = \text{Br}, \text{I}$) is treated with H_3PO_4 and not by concentrated H_2SO_4 since,
 (1) Na_3PO_4 is water insoluble and Na_2SO_4 is water soluble
 (2) Na_2SO_4 is water soluble and Na_3PO_4 is water insoluble
 (3) H_2SO_4 oxidizes HX to X_2 (Br_2, I_2)
 (4) H_2SO_4 makes the reaction reversible
94. The reaction of KMnO_4 and HCl results in
 (1) Reduction of Mn in KMnO_4 and production of Cl_2
 (2) Oxidation of Mn in KMnO_4 and production of H_2
 (3) Reduction of Mn in KMnO_4 and production of H_2
 (4) Oxidation of Mn in KMnO_4 and production of Cl_2
95. $\text{NaCl} + \text{A} \longrightarrow \text{NaNO}_3 + \text{B} + \text{Cl}_2 + \text{H}_2\text{O}$
 $\text{B} + \text{O}_2 \longrightarrow \text{C} + \text{Cl}_2$
 $\text{C} + \text{O}_2 + 2\text{H}_2\text{O} \longrightarrow \text{A}$
 A, B and C are
 (1) $\text{AgNO}_3, \text{NaOCl}, \text{N}_2\text{O}_4$ (2) $\text{HNO}_3, \text{NOCl}, \text{NO}_2$
 (3) $\text{HNO}_3, \text{NaOCl}, \text{NO}$ (4) $\text{AgNO}_3, \text{NOCl}, \text{NO}_2$
96. The inter-halogen compound not obtained is
 (1) BrCl_7 (2) BrF_5
 (3) IF_5 (4) ICl
97. Which of the underlined atoms in oxyacids have sp hybridized atoms?
 (1) $\text{HClO}_4, \text{HNO}_3, \text{HClO}_3$ (2) $\text{HClO}_4, \text{H}_2\text{SO}_4, \text{H}_2\text{SO}_5$
 (3) $\text{H}_2\text{SO}_4, \text{H}_2\text{PO}_4, \text{HNO}_3$ (4) $\text{HClO}_4, \text{H}_2\text{SO}_4, \text{HNO}_2$
98. Auto oxidation of bleaching powder gives:
 (1) Only calcium chlorate (2) Only calcium hypochlorite
 (3) Only calcium chloride (4) Both (1) and (3)
99. Which is incorrectly matched?
 (1) $\text{I}_4\text{O}_9 \rightleftharpoons \text{I}^{3+} + 3\text{IO}_3^-$ (2) $\text{CsBr}_3 \rightleftharpoons \text{Cs}^+ + \text{Br}_3^-$
 (3) $\text{I}_2\text{O}_4 \rightleftharpoons \text{IO}^+ + \text{IO}_3^-$ (4) None of these
100. The incorrect order is:
 (1) $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$: Bond dissociation enthalpy
 (2) $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$: Boiling point
 (3) $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$: Thermal stability
 (4) $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$: Acidic strength
101. Concentrated H_2SO_4 cannot be used to prepare HBr from NaBr , because it:
 (1) reacts slowly with NaBr (2) Disproportionates HBr
 (3) Oxidises HBr (4) Reduces HBr
102. A greenish yellow gas reacts with an alkali metal hydroxide to form a halite which can be used in fire works and safety matches. The gas and halite respectively are:
 (1) $\text{Br}_2, \text{KBrO}_3$ (2) $\text{Cl}_2, \text{KClO}_3$
 (3) $\text{I}_2, \text{NaIO}_3$ (4) None
103. Which of the following is an inter-pseudo-halogens (Pseudo-halogen analogues of inter-halogen)?
 (1) C_2N_2 (2) BrF_5
 (3) ICN (4) HSCN
104. A dark violet solid X reacts with NH_3 to form a mild explosive which decomposes to give a violet coloured gas. X also reacts with H_2 to give an acid Y. Y can also be prepared by heating its salt with H_3PO_4 . X and Y are:

- (1) Cl_2 , HCl
 (3) Br_2 , HBr
105. In the reaction,
 $3\text{Br}_2 + 6\text{CO}_3^{2-} + 3\text{H}_2\text{O} \longrightarrow 5\text{Br}^- + \text{BrO}_3^- + 6\text{HCO}_3^-$
 (1) Bromine is neither oxidized nor reduced
 (2) Bromine is both oxidized and reduced
 (3) Bromine is reduced and water is oxidized
 (4) Bromine is oxidized and carbonate is reduced
106. Which of the following does not decolourise iodine?
 (1) Na_2SO_3 (2) NaCl
 (3) $\text{Na}_2\text{S}_2\text{O}_3$ (4) NaOH
107. Ammonia and chlorine are made to react. If ammonia is in excess, products formed are A and B and when chlorine is in excess the products are C and D. A, B, C and D are
 (1) N_2 , NH_4Cl and NCl_3 , HCl
 (2) N_2 , HCl and N_2 , NH_4Cl
 (3) N_2 , NH_4Cl and NCl_3 , HCl
 (4) NCl_3 , HCl and N_2 , NH_4Cl
108. Inter-halogen compound which exists in dimeric form, is:
 (1) ICl_3 (2) ICl
 (3) IF_7 (4) BrF_5

Multiple Correct Answers Type

Physical and Chemical Properties of Halogens

- Which one of the following arrangements does not give the correct picture of the trends indicated against it?
 (1) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$: Bond dissociation energy
 (2) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$: Oxidising power
 (3) $\text{F} > \text{Cl} > \text{Br} > \text{I}$: Electron gain enthalpy
 (4) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$: Electronegativity
- Which one of the following halogens turn(s) starch iodide paper blue?
 (1) Cl_2 (2) Br_2
 (3) I_2 (4) F_2
- Which one of the following salts will evolve halogen on treatment with conc. H_2SO_4 ?
 (1) NaCl (2) CaCl_2
 (3) NaBr (4) KI
- Electrolysis of aqueous solution of Brine (NaCl) gives
 (1) Cl_2 (2) H_2
 (3) NaOH (4) None of these
- The halogens, which are not attacked by conc. HNO_3 , are
 (1) F_2 (2) Cl_2
 (3) Br_2 (4) I_2
- Select the correct order:
 (1) $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ (2) $\text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$
 (3) $\text{HClO} < \text{HBrO} < \text{HIO}$ (4) None of these
- Which one of the following reactions does not occur?
 (1) $\text{F}_2 + 2\text{Cl}^- \longrightarrow 2\text{F}^- + \text{Cl}_2$ (2) $\text{Cl}_2 + 2\text{F}^- \longrightarrow 2\text{Cl}^- + \text{F}_2$
 (3) $\text{Br}_2 + 2\text{I}^- \longrightarrow 2\text{Br}^- + \text{I}_2$ (4) $\text{I}_2 + 2\text{Br}^- \longrightarrow \text{Br}_2 + 2\text{I}^-$
- Identify the correct statements:
 (1) SCN^- is a pseudohalide
 (2) Iodine shows Lewis basic nature
 (3) AgF is insoluble in water
 (4) Fluorine is a super halogen
- Which of the following properties of the elements chlorine, bromine and iodine increases with increasing atomic number?
 (1) Enthalpy of vaporization
 (2) Ionic radius
 (3) Bond energy of the molecule X_2
 (4) Ionization energy
- Predict product(s) in the following reaction
 $\text{Cl}_2 + \text{OH}^- \xrightarrow{\text{hot}} ?$
 (1) ClO_3^- (2) OCl^-
 (3) ClO_2^- (4) Cl^-
- Which of the following statement(s) is/are correct for Halogens?
 (1) The strongest oxidizing agent is iodine
 (2) The most reactive halogen is fluorine
 (3) The most electronegative element is fluorine
 (4) Halogen which is liquid at room temperature is bromine
- Select the correct statement(s)
 (1) Chile saltpeter (NaNO_3) is a main source of I_2
 (2) IO_3^- is reduced to I^- and which in turn oxidized to I_2 by IO_3^- in acidic medium
 (3) Anhydrous HF is a non-conductor of electricity
 (4) F_2 is obtained by electrolysis of molten KHF_2
- Select the incorrect statement(s)
 (1) NF_3 has a highest dipole moment among CO , NH_3 and NF_3
 (2) HClO_3 is weakest acid among HIO_3 , HBrO_3 and HClO_3
 (3) Cl_2 has a lowest boiling point among Cl_2 , Br_2 and I_2
 (4) HF has a highest boiling point among CH_4 , NH_3 and HF
- Base on the values given, select correct statements

$$\frac{1}{2}\text{F}_2 + e^- \longrightarrow \text{F}^- \quad E^\circ = 2.87 \text{ V}$$

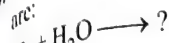
$$\frac{1}{2}\text{Cl}_2 + e^- \longrightarrow \text{Cl}^- \quad E^\circ = 1.40 \text{ V}$$

$$\frac{1}{2}\text{Br}_2 + e^- \longrightarrow \text{Br}^- \quad E^\circ = 1.09 \text{ V}$$

$$\frac{1}{2}\text{I}_2 + e^- \longrightarrow \text{I}^- \quad E^\circ = 0.62 \text{ V}$$
 (1) Oxidizing power is in order $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$
 (2) Oxidizing power is in order $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
 (3) Oxidizing power of I_2 is maximum
 (4) Oxidizing power of F_2 is maximum
- All the halogens are coloured and the colour changes with increasing size of the halogen molecule. It is due to
 (1) adsorption of light in the visible region

- (2) transition from π^* to σ^* molecular orbital
 (3) transition from π to π^* molecular orbital
 (4) none of these
16. In correct statements about the hydrogen halides include that:
 (1) They are all coloured
 (2) The thermal stability decreases with increasing atomic number of halogen
 (3) They all form soluble silver salts
 (4) They all donate protons to water
17. Select the correct statement(s)
 (1) pK_a value of HI (strongest halogen acid) is most negative
 (2) High H—F bond strength makes H—F a weak acid in dilute aqueous solution
 (3) Halogen forms clathrates by freezing solution in water
 (4) K_a values of HX is in order $HF < HCl < HBr < HI$
18. Which of the following arrangements represent correctly the property indicated against it.
 (1) $Br < Cl < F$: Electron affinity
 (2) $Br_2 < Cl_2 < F_2$: Oxidizing power
 (3) $Br < Cl < F$: Electronegativity
 (4) $Br_2 < Cl_2 < F_2$: Bond energy
19. In the isolation of fluorine a number of difficulties were encountered. Which statements are correct?
 (1) Fluorine reacts with moist glass vessels
 (2) Fluorine has great affinity for hydrogen
 (3) Electrolysis of aqueous HF gives ozonized oxygen
 (4) The potential required for the discharge of the fluoride ions lowest
20. Iodine is formed when potassium iodide reacts with:
 (1) $ZnSO_4$ (2) $CuSO_4$
 (3) Cl_2 (4) Br_2
21. Select the correct order(s)
 (1) $HOCl > HOBr > HOI$ – acid strength
 (2) $HClO_4 < HClO_3 < HClO_2 \leq HClO$ – oxidizing power
 (3) $ClO_4^- < BrO_4^- > IO_4^-$ – oxidizing power
 (4) $IO^- > BrO^- > ClO^-$ – ease of disproportionation
22. Select the correct ones
 (1) BrO_2 upon alkaline hydrolysis gives bromide and bromate
 (2) It converts benzene to 1,4-diquinone
 (3) It converts I_2 to I_2O_5
 (4) Br_2O is a dark brown solid and is highly oxidizing
23. Iodine reacts with hypo to give:
 (1) NaI (2) $Na_2S_4O_6$
 (3) Na_2SO_3 (4) Na_2SO_4
24. Chlorine reacts with
 (1) N_2 (2) O_2
 (3) S_8 (4) Fe
25. Which oxidation state of Cl is observed when Cl_2 reacts with hot and conc. NaOH solution?
 (1) +1 (2) -1
 (3) +5 (4) +7
26. If Y_2 in given reaction is Cl_2 then “X” is/are:
 (1) I (2) Br
 (3) Cl (4) F
 $Y_2 + 2X_{(aq)}^{(1)} \longrightarrow 2Y_{(aq)}^{(2)} + X_2$
27. Available chlorine is liberated from bleaching powder when it
 (1) reacts with CO_2 (2) reacts with acid
 (3) reacts with H_2O (4) is heated
28. Species which are isoelectronic with OF_2 are
 (1) ClO^\ominus (2) ClF
 (3) ClO_3 (4) ClO_2
29. HI cannot be prepared by the action of conc. H_2SO_4 on K because
 (1) HI is stronger acid than H_2SO_4
 (2) H_2SO_4 is stronger oxidising agent than HI
 (3) H_2SO_4 is an oxidising agent
 (4) HI is a strong reducing agent
30. Select triangular planar species among the following:
 (1) ClO_3^\ominus (2) H_3O^\oplus
 (3) CH_3^\oplus (4) ClO_2^\ominus
31. Iodine reacts with hypo to give
 (1) NaI (2) Na_2SO_3
 (3) $Na_2S_4O_6$ (4) Na_2SO_4
32. Which one of the following are pseudohalide ions?
 (1) CNO^\ominus (2) OCN^\ominus
 (3) $RCOO^\ominus$ (4) N_3^\ominus
33. Cl_2 reacts with hot aqueous NaOH to give
 (1) NaCl (2) $NaClO_3$
 (3) $NaClO_2$ (4) $NaClO_4$
34. Aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 gives
 (1) $Na_2S_4O_6$ (2) $NaHSO_4$
 (3) HCl (4) NaOH
35. Which of the following statements are correct?
 (1) Bleaching powder converts acetone or ethyl alcohol into chloroform
 (2) The maximum percentage of available chlorine is calculated from iodine's formula is 49%
 (3) Thermal stability of $KI_3 < NaI_3$
 (4) Thermal stability for trihalides formed by same metal is $I_3^- > IBr_2^- > ICl_2^- > I_2Br^- > Br_3^- > BrCl_2^- > Br_2Cl^-$
36. Hypoiodous acid is formed with
 (1) KOH (2) HgO
 (3) C_2H_5OH (4) I_2
37. Which of the following product(s) is/are obtained when Cl_2O_6 reacts with NaOH?
 (1) $KClO_4$ (2) $KClO_3$
 (3) $KClO_2$ (4) KCl
38. Which of the following species does/do not exist?
 (1) ICl_3^\oplus (2) NCl_5
 (3) NH_2^\oplus (4) OF_4

39. The possible product(s) formed in the following reaction is/are:



- (1) HF (2) HIO_2
(3) HIO (4) HIO_3

40. Which of the following reaction(s) do/does not give an oxo-acid?

- (1) Two moles of nitric acid $\xrightarrow{-\text{H}_2\text{O}}$
(2) One mole of sulphuric acid $\xrightarrow{-\text{H}_2\text{O}}$
(3) Two moles of perchloric acid $\xrightarrow{-\text{H}_2\text{O}}$
(4) Two moles of sulphuric acid $\xrightarrow{-\text{H}_2\text{O}}$

41. Correct order(s) is/are:

- (1) $\text{X}-\text{C}-\text{N}$ bond angle: $\text{COCl}_2 > \text{COF}_2$
(2) Melting point: $\text{NH}_3 < \text{SbH}_3 < \text{AsH}_3 < \text{PH}_3$
(3) Bond dissociation energy: $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$
(4) Thermal stability: $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$

42. Which reactions are used for the preparation of the halogen acid?

- (1) $2\text{KI} + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{HI}$
(conc.)
(2) $\text{CaF}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + 2\text{HF}$
(conc.)
(3) $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl}$
(conc.)
(4) $2\text{KBr} + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{HBr}$
(conc.)

43. Which of the following statements are correct?

- (1) Fluorine compounds are more stable than corresponding chlorine compounds
(2) Fluorine forms oxysalt when it reacts with alkalis while other halogens do not
(3) F_2 undergoes disproportionation reaction in the alkaline medium while other halogens do not
(4) Due to hydrogen bonding HF can form acid salts of the type $[\text{K}^+(\text{F}-\text{H}-\text{F})^-]$

44. Which of the following statement(s) is/are correct?

- (1) ClO_2 is a yellow gas but deep red liquid
(2) ClO_2 is diamagnetic in nature
(3) ClO_2 in alkaline solution undergoes disproportionation
(4) Chlorine dioxide (ClO_2) is powerful oxidizing agent but bleaching action is lower than Cl_2

45. Which of the following statements is true about NO_2 and ClO_2 ?

- (1) In both oxides, the central atom has an oxidation state +4
(2) On cooling, both undergo dimerization
(3) Both have a bent structure
(4) Both are paramagnetic

46. $\text{Cl}_2\text{O}_6 + \text{NaOH} \longrightarrow ?$

- (1) NaClO_3 (2) NaClO_2
(3) NaOCl (4) NaClO_4

47. Select the

- (1) F_2 forms F_3^\ominus ion and I_2 forms I_3^\ominus ion
(2) ClF_3 exists but FCl_3 does not
(3) Alkaline KMnO_4 oxidises I_2 to I^\ominus
(4) F_2 forms only one oxo acid.

48. Select the incorrect statements

- (1) Both NO and ClO_2 dimerise
(2) Addition of excess of Cl_2 to KI solution gives colourless solution
(3) H_2SO_4 is stronger acid than HClO_4
(4) Inter-halogen compounds are more reactive than halogens

Linked Comprehension Type

Paragraph 1

Fluorine, the first member of group 17, differs from the other members of the group in many respects due to:

- Very small size
- Very high electronegativity
- Absence of vacant d -orbitals in the valence shell
- Dissociation energy in the molecular form (X_2) is the least

1. Which member of the group 17 does not show positive oxidation state?

- (1) Iodine (2) Bromine
(3) Chlorine (4) Fluorine

2. Which has the maximum molar enthalpy of vaporisation?

- (1) HF (2) HCl
(3) HBr (4) HI

3. Which of the following bonds is the strongest?

- (1) $\text{F}-\text{F}$ (2) $\text{Cl}-\text{Cl}$
(3) $\text{Br}-\text{Br}$ (4) $\text{I}-\text{I}$

4. Which halogen does not form any oxyacid?

- (1) Iodine (2) Bromine
(3) Chlorine (4) Fluorine

5. The most basic among the following is:

- (1) Cl^\ominus (2) Br^\ominus
(3) F^\ominus (4) I^\ominus

6. Which of the following do not exist?

- (1) IF (2) FCl_3
(3) IF_3 (4) IF_5

Paragraph 2

Halogens react with each other to form a number of compounds called interhalogen compounds. Their general formula is AX_n , where A is less electronegative halogen while X is a more electronegative halogen and n is its number. The interhalogen compounds are essentially covalent and more reactive than the halogens since the bond $\text{A}-\text{X}$ is weaker than $\text{A}-\text{A}$ or $\text{X}-\text{X}$ bond. The reactions of interhalogens are similar to those of halogens.

7. Which of the following interhalogen compound is not possible?

- (1) IF_7 (2) IF_5
(3) ClF_3 (4) FBr_3

8. Which halogen shows maximum oxidation state in forming interhalogen compound?

- (1) I (2) Br
(3) Cl (4) F

9. How many lone pairs of electrons are present on chlorine in ClF_3 molecule?

- (1) 0 (2) 1
(3) 2 (4) 3

10. Which of the following statement is wrong for inter-halogen?

- (1) The value of n in AX_n (interhalogen) can be 1, 3, 5 or 7
(2) The value of n in AX_n (interhalogen) can be 2, 4, or 6
(3) A can never be fluorine as it is most electronegative halogen.
(4) X can never be iodine as it is least electronegative halogen.

Paragraph 3

I_2 has less solubility in water and its solubility increases on adding KI solution. When KI and I_2 react then a species 'X' is formed by which solubility of I_2 increases.

11. Hybridisation of anionic part of 'X' is

- (1) sp^2 (2) sp^3
(3) sp^3d (4) sp^3d^2

12. Shape of anionic part of 'X' is

- (1) Linear (2) T shape
(3) Pyramidal (4) See-saw

13. Which of the following is the correct characteristic of anionic part of 'X'?

[Polar and non-polar nature to be considered on the basis of dipole moment]

- (I) Planar (II) non-planar (III) Polar (IV) non-polar
(1) I and III (2) I and IV
(3) II and III (4) II and IV

14. Geometry of anionic part of X is

- (1) Trigonal bipyramidal (2) Square pyramidal
(3) Pentagon (4) Linear

Paragraph 4

Oxygen is more electronegative than chlorine. In the series of oxyacids HOCl , HClO_2 , HClO_3 and HClO_4 , an increasing number of oxygen atom is bonded to the chlorine atom.

Chlorine forms a number of oxyacids which differ in their strengths. The conjugate base of these acids also differs in their stability order.

15. The order of acidic strength of HOCl , HClO_2 , HClO_3 and HClO_4 are

- (1) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$
(2) $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$
(3) $\text{HClO}_3 > \text{HClO}_4 > \text{HClO}_2 > \text{HOCl}$
(4) $\text{HClO}_3 > \text{HClO}_2 > \text{HOCl} > \text{HClO}_4$

16. Which of the following is the strongest conjugate base?

- (1) ClO^\ominus (2) ClO_2^\ominus
(3) ClO_3^\ominus (4) ClO_4^\ominus

17. The hybridisation of Cl in ClO_2 and its shape are

- (1) sp^3 , pyramidal (2) sp^2 , angular
(3) sp^3 , angular (4) sp^2 , trigonal planar

18. The least stable oxo-anion among the following is

- (1) ClO^\ominus (2) ClO_2^\ominus
(3) ClO_3^\ominus (4) ClO_4^\ominus

Paragraph 5

Among the halogens, fluorine differs considerably from the other members. The hydrides of halogens also differ in their properties.

19. Fluorine differs from the other halogens due to:

- (1) Small size
(2) Very high electronegativity
(3) Non-availability of d -orbitals
(4) All of these

20. Which of the following bond has the highest bond energy?

- (1) F-F (2) Cl-Cl
(3) Br-Br (4) I-I

21. Which of the following halogens do not form polyhalide?

- (1) F (2) Cl
(3) Br (4) I

Paragraph 6

Bleaching powder is a mixed salt of hydrochloric acid and hypochlorous acid. It has the formula, $\text{CaOCl}_2 \cdot \text{H}_2\text{O}$. It is manufactured by the action of chlorine on dry slaked lime at 40°C . There is also a view that bleaching powder is a mixture of calcium hypochlorite and basic calcium chloride, $[\text{Ca}(\text{OCl})_2 + \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}]$.

The amount of chlorine obtained from a sample of bleaching powder by the treatment with excess of dilute acids or CO_2 is called available chlorine. A good sample of bleaching powder contains 35–38% of available chlorine. On long standing, it undergoes auto-oxidation and the amount of available chlorine decreases.

The estimation of available chlorine is done volumetrically by (a) iodometric method or by (b) arsenite method.

In textile industry, the cotton cloth is mainly bleached with the help of bleaching powder.

22. Maximum percentage of available chlorine on the basis of $\text{CaOCl}_2 \cdot \text{H}_2\text{O}$ formula is

- (1) 35 (2) 40
(3) 45 (4) 49

23. On long standing, the bleaching powder undergoes auto-oxidation. The products formed are

- (1) Calcium chloride only
(2) Calcium chlorate only
(3) Calcium chloride and calcium chlorate
(4) Calcium chloride and calcium chlorite

24. The chemical name of bleaching powder is

- (1) Calcium hypochlorite
(2) Calcium chlorohypochlorite
(3) Calcium chlorate
(4) Calcium perchlorate

The percentage of available chlorine in commercial samples of bleaching powder is usually between 35% and 38%. The low value is due to

- Incomplete reaction between slaked lime and Cl_2 during its formation.
- Impurities present in the original slaked lime.
- Decomposition of bleaching powder when kept in air.
- All of the above.

28. 3.55 g of bleaching powder when treated with acetic acid and excess of KI liberated iodine which required 60 mL of 0.5 N sodium thiosulphate solution. The percentage of available chlorine in the sample is

- 30.0
- 25.0
- 20.0
- 35.0

Matrix Match Type

This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

Column I	Column II
a. I_2O_5	i. Liquid at room temperature
b. ClO_2	ii. Used in estimation of CO
c. Br_2	iii. Paramagnetic
d. O_2	iv. Powerful bleaching agent

Column I	Column II
a. I^\ominus	i. Pseudo halide
b. CN^\ominus	ii. Gives compound with Cu^{+2} via redox reaction
c. HClO_4	iii. Reacts with HF
d. HOCl	iv. Acid anhydride

Column I	Column II
a. Deacon process	i. Isolation of F_2
b. Baeyer process	ii. Manufacture of HNO_3
c. Moissan method	iii. Manufacture of Cl_2
d. Ostwald process	iv. Purification of bauxite

Column I	Column II
a. Corrosive liquid	i. F_2
b. Maximum solubility in water	ii. Cl_2
c. Maximum bond dissociation energy	iii. Br_2
d. Maximum inter-atomic distance	iv. I_2

II. Match the items given in Column I with that in Column II and III

Column I	Column II	Column III
Interhalogen compound	Characteristics (I)	Characteristics (II)
a. IF	i. Undergo hydrolysis to give periodic acid	p. sp^3d , arrow shape, 2 lp
b. IF_3	ii. Undergo hydrolysis to give hypoiodous acid	q. sp^3 , linear, 3 lp
c. IF_5	iii. Undergo hydrolysis to give iodic acid	r. sp^3d^3 , pentagonal bipyramidal, zero lp
d. IF_7	iv. Undergo hydrolysis to give iodic acid	s. sp^3d^2 , square pyramid, 1 lp

Column I	Column II
a. Bleaching powder	i. HF
b. Pseudohalogen	ii. IBr_3
c. Interhalogen compound	iii. $(\text{CN})_2$
d. Hydrogen bonding	iv. CaOCl_2

Column I (Interhalogen compound)	Column II (Hybridisation of I)
a. ICl	i. sp^3d
b. ICl_3	ii. sp^3d^3
c. ICl_5	iii. sp^3d^2
d. ICl_7	iv. sp^3

Column I	Column II
a. Fluorspar	i. Na_3AlF_6
b. Cryolite	ii. AgCl
c. Apatite	iii. CaF_2
d. Horn silver	iv. $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$

Column I	Column II
a. Carnalite	i. KCl
b. Sylvine	ii. Ash obtained on burning sea-weeds which contains 1% iodine as iodine of alkali metal
c. Kelp	iii. $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
d. Caliche	iv. Contains iodine as sodium iodate

Column I	Column II
a. HOCl	i. Perhalic acid
b. HClO_2	ii. Halous acid
c. HClO_3	iii. Hypohalous acid
d. HClO_4	iv. Halic acid

Column I	Column II
a. Fermy's salt	i. KClO_3
b. Javelle water	ii. KHF_2
c. Berthelot's salt	iii. Aqueous solution of NaOCl
d. Anhydrone	iv. Anhydrous magnesium perchlorate

For Q.12 to Q.15

Answer the questions given below by appropriately matching the information given in three Column of the following table.

Column I		Column II		Column III	
E.C. of Halogens		Characteristics (I)		Characteristics (II)	
a.	$4s^2 4p^5$	i.	Highest electron gain enthalpy	p.	It is used in the preparation of photosensitive papers, films and plates
b.	$5s^2 5p^5$	ii.	Highest electronegativity	q.	Pale yellow
c.	$2s^2 2p^5$	iii.	It does not dissolve in water. It is more soluble in Csl solution than in pure water	r.	Brown red
d.	$3s^2 3p^5$	iv.	It is obtained from mother liquor obtained from crystallisation of carnalite (called Bittern)	s.	It is used in preparation of poisonous gases like phosgene, tear and mustard gases.

12. For chlorine, CORRECT combination is:

- (1) a—iv—r (2) d—i—s
(3) c—ii—q (4) d—i—p

13. For fluorine, CORRECT combination is:

- (1) c—ii—q (2) c—ii—r
(3) d—i—s (4) d—i—p

14. For bromine, CORRECT combination is:

- (1) a—iv—r (2) a—iv—q
(3) b—iii—p (4) b—iii—s

15. For iodine, CORRECT combination is:

- (1) a—iv—r (2) a—iv—q
(3) b—iii—p (4) b—iii—s

Numerical Value Type

- Sodium iodate is treated with calculated amount of sodium bisulphite to prepare iodine. How many moles of sodium bisulphite are required to prepare one mole of iodine from sodium iodate?
- In the molecule ICl_3 , how many lone pairs of electrons are associated with iodine?

3. In the interhalogen compound AB_n , what is the maximum value of n ?4. In a given sample of bleaching powder, the percentage of available chlorine is 49. The volume in litres of chlorine obtained if 20 g of the sample is treated with HCl at NTP is.5. What is the oxidation state of iodine in H_5IO_6 ?6. How many orbitals are involved in the hybridisation of iodine in IF_7 ?7. Chlorine water on cooling deposits greenish yellow crystals of formula $\text{Cl}_2 \cdot \text{XH}_2\text{O}$. What is the value of X ?8. How many lone pairs are associated with I in IF_7 ?9. What is the oxidation state of Cl in HClO_4 ?10. What is the oxidation state of Cl in HClO_4 ?

11. For oxyacid HClO_x , If $x = y = z$ (x , y and z are natural numbers), then calculate the value of $(x + y - z)$ where
 x = Total number of lone pair on central atom.
 y = Total number of $\pi - e^-$'s in the oxyacid.
 z = Total number of 'O' atoms.

12. Covalency of chlorine atom in second excite state is.

Archives**JEE MAIN****Single Correct Answer Type**

- Which of the following exists as covalent crystals in the solid state?
 (1) Iodine (2) Silicon
 (3) Sulphur (4) Phosphorus

(JEE Main 2013)

2. The correct statement for the molecule CsI_3 is

- (1) It contains Cs^+ and I^- ions
 (2) It contains Cs^+ and I^- and lattice I_2 molecule
 (3) It is a covalent molecule
 (4) It contains Cs^+ and I_3^- ions

(JEE Main 2014)

3. Among the following oxoacids, the correct decreasing order of acid strength is

- (1) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$
 (2) $\text{HClO}_2 > \text{HClO}_4 > \text{HClO}_3 > \text{HOCl}$
 (3) $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$
 (4) $\text{HClO}_4 > \text{HOCl} > \text{HClO}_2 > \text{HClO}_3$

(JEE Main 2014)

4. Which among the following is the most reactive?

- (1) Cl_2 (2) Br_2
 (3) I_2 (4) ICl

(JEE Main 2015)

4. Order the processes in the correct processes.

- (a) Wacker process
(b) Ziegler-Natta polymerization
(c) Contact process
(d) Deacon's process
- (i) (S) = (ii), (C) = (iv), (D) = (i)
(ii) (S) = (i), (C) = (iv), (D) = (iii)
(iii) (S) = (iii), (C) = (iv), (D) = (i)
(iv) (S) = (i), (C) = (ii), (D) = (iv)

(JEE Main 2015)

ADVANCED

Single Correct Answer Type

Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively is acting as a

- (1) Reducing agent, oxidising agent
(2) Reducing agent, reducing agent
(3) Oxidising agent, oxidising agent
(4) Oxidising agent, reducing agent

(JEE Advanced 2014)

5. Which among the following is the most reactive?

- (1) Cl_2 (2) Br_2
(3) I_2 (4) ICl

(JEE Advanced 2015)

Multiple Correct Answers Type

1. The reagent(s) used for softening the temporary hardness of water is/are

- (1) $\text{Ca}_3(\text{PO}_4)_2$ (2) $\text{Ca}(\text{OH})_2$
(3) Na_2CO_3 (4) NaOCl

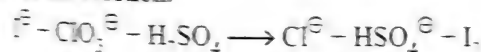
(IIT-JEE 2010)

2. Which of the following halides react(s) with $\text{AgNO}_3(\text{aq})$ to give a precipitate that dissolves in $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$

- (1) HCl (2) HF
(3) HBr (4) HI

(IIT-JEE 2012)

3. For the reaction:



The correct statement(s) in the balanced equation is/are

- (1) Stoichiometric coefficient of HSO_4^- is 6.
(2) Iodide is oxidised.
(3) Sulphur is reduced.
(4) H_2O is one of the products.

(JEE Advanced 2014)

4. The correct statement(s) regarding, (i) HClO , (ii) HClO_2 , (iii) HClO_3 and (iv) HClO_4 is (are)

- (1) The number of $\text{Cl}=\text{O}$ bonds in (ii) and (iii) together is two
(2) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three
(3) The hybridization of Cl in (iv) is sp^3

(4) Amongst (i) to (iv), the strongest acid is (i)

(JEE Advanced 2015)

5. The correct statement(s) about the oxoacids, HClO_4 and HClO , is(are)

- (1) HClO_4 is more acidic than HClO because of the resonance stabilization of its anion
(2) HClO_4 is formed in the reaction between Cl_2 and H_2O
(3) The central atom in both HClO_4 and HClO is sp^2 hybridized
(4) The conjugate base of HClO_4 is weaker base than H_2O

(JEE Advanced 2017)

6. The colour of the X_2 molecule of group 17 elements changes gradually from yellow to violet down the group. This due to

- (1) the physical state of X_2 at atom temperature changes from gas to solid down the group
(2) decrease in HOMO-LUMO gap down the group
(3) decrease in $\pi^*-\sigma^*$ gap down the group
(4) decrease in ionization energy down the group

(JEE Advanced 2017)

Linked Comprehension Type

Paragraph 1

Bleaching powder and bleach solution are produced on a large scale and used in several house hold production. The effectiveness of bleach solution is often measured by iodometry.

1. 25 mL of household beach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4N acetic acid. In the titration of the liberated I_2 , 48 mL of 0.25 N $\text{Na}_2\text{S}_2\text{O}_3$ was used to reach the end point. The molarity of the household bleach solution is

- (1) 0.48 M (2) 0.96 M
(3) 0.24 M (4) 0.024 M

2. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is

- (1) Cl_2O (2) Cl_2O_7
(3) ClO_2 (4) Cl_2O_8

(IIT-JEE 2012)

Paragraph 2

The reactions of Cl_2 gas with cold-dilute and hot-concentrated NaOH in water give sodium salts of two different oxoacids of chlorine, P and Q, respectively. The Cl_2 gas reacts with SO_2 gas, in presence of charcoal, to give a product R reacts with white phosphorus to give a compound S. On hydrolysis, S gives an oxoacid of phosphorus.

3. P and Q, respectively, are the sodium salts of

- (1) Hypochlorous and chloric acids
(2) Hypochlorous and chlorous acids
(3) Chloric and perchloric acids
(4) Chloric and hypochlorous acids.

4. R, S and T, respectively, are

- (1) SO_2Cl_2 , PCl_5 and H_3PO_4 (2) SO_2Cl_2 , PCl_3 and H_3PO_3
(3) SOCl_2 , PCl_3 and H_3PO_2 (4) SOCl_2 , PCl_5 and H_3PO_4

(JEE Advanced 2013)

Matrix Match Type

This section contains questions each with two columns-I and II. Match the items given in column I with that in column II.

1. The unbalanced chemical reactions given in Column I show missing reagent or condition (?) which are provided in Column II. Match Column I with Column II and select the correct answer using the code given below:

Column I		Column II	
P.	$\text{PbO}_2 + \text{H}_2\text{SO}_4 \xrightarrow{?} \text{PbSO}_4 + \text{O}_2 + \text{Other product}$	1.	NO
Q.	$\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \xrightarrow{?} \text{NaHSO}_4 + \text{other product}$	2.	I_2
R.	$\text{N}_2\text{H}_4 \xrightarrow{?} \text{N}_2 + \text{other product}$	3.	Warm
S.	$\text{XeF}_2 \xrightarrow{?} \text{Xe} + \text{other product}$	4.	Cl_2

Codes:

	P	Q	R	S
(1)	4	2	3	1
(2)	3	2	1	4
(3)	1	4	2	3
(4)	3	4	2	1

Numerical Value Type

- Based on VSEPR theory, the number of 90 degree F-Br-F angles in BrF_5 is _____. (IIT-JEE 2010)
- Reaction of Br_2 with Na_2CO_3 in aqueous solution gives NaBr and sodium bromate with evolution of CO_2 gas. The number of NaBr molecule involved in the balanced chemical equation is _____. (IIT-JEE 2011)
- Consider the following list of reagents: Acidified $\text{K}_2\text{Cr}_2\text{O}_7$, alkaline KMnO_4 , CuSO_4 , H_2O_2 , Cl_2 , O_3 , HNO_3 and $\text{Na}_2\text{S}_2\text{O}_3$. The total number of reagents that can oxidise aqueous I^- ion I_2 is _____ (JEE Advanced 2014)

Answers Key**EXERCISES****Single Correct Answer Type**

- | | | | | |
|----------|----------|----------|----------|----------|
| 1. (2) | 2. (1) | 3. (1) | 4. (3) | 5. (1) |
| 6. (3) | 7. (1) | 8. (4) | 9. (2) | 10. (1) |
| 11. (4) | 12. (2) | 13. (4) | 14. (1) | 15. (4) |
| 16. (4) | 17. (1) | 18. (3) | 19. (1) | 20. (2) |
| 21. (4) | 22. (1) | 23. (1) | 24. (3) | 25. (2) |
| 26. (4) | 27. (3) | 28. (2) | 29. (3) | 30. (3) |
| 31. (3) | 32. (4) | 33. (2) | 34. (4) | 35. (4) |
| 36. (3) | 37. (3) | 38. (2) | 39. (1) | 40. (1) |
| 41. (3) | 42. (1) | 43. (1) | 44. (4) | 45. (1) |
| 46. (2) | 47. (3) | 48. (2) | 49. (1) | 50. (1) |
| 51. (2) | 52. (3) | 53. (3) | 54. (2) | 55. (2) |
| 56. (1) | 57. (1) | 58. (1) | 59. (2) | 60. (1) |
| 61. (3) | 62. (1) | 63. (2) | 64. (4) | 65. (1) |
| 66. (3) | 67. (1) | 68. (2) | 69. (3) | 70. (4) |
| 71. (4) | 72. (2) | 73. (1) | 74. (3) | 75. (4) |
| 76. (1) | 77. (4) | 78. (4) | 79. (1) | 80. (3) |
| 81. (2) | 82. (2) | 83. (2) | 84. (1) | 85. (1) |
| 86. (1) | 87. (3) | 88. (1) | 89. (1) | 90. (2) |
| 91. (2) | 92. (2) | 93. (3) | 94. (1) | 95. (2) |
| 96. (1) | 97. (2) | 98. (4) | 99. (4) | 100. (2) |
| 101. (3) | 102. (3) | 103. (3) | 104. (3) | 105. (2) |
| 106. (2) | 107. (3) | 108. (1) | | |

Multiple Correct Answers Type

- | | | |
|--------------|--------------|--------------|
| 1. (1, 3) | 2. (1, 2) | 3. (3, 4) |
| 4. (1, 2, 3) | 5. (1, 2, 3) | 6. (1, 2, 4) |

- | | | |
|------------------|------------------|------------------|
| 7. (2, 4) | 8. (1, 4) | 9. (1, 2) |
| 10. (1, 4) | 11. (2, 3, 4) | 12. (1, 2, 3, 4) |
| 13. (1, 2) | 14. (2, 4) | 15. (1, 2) |
| 16. (1, 3) | 17. (1, 2, 3, 4) | 18. (2, 3) |
| 19. (1, 2, 3) | 20. (2, 3, 4) | 21. (1, 2, 4) |
| 22. (1, 2, 3, 4) | 23. (1, 2) | 24. (3, 4) |
| 25. (2, 3) | 26. (1, 2) | 27. (1, 2) |
| 28. (1, 2) | 29. (1, 3, 4) | 30. (3, 4) |
| 31. (1, 3) | 32. (1, 2) | 33. (1, 2) |
| 34. (2, 3) | 35. (1, 2, 4) | 36. (2, 4) |
| 37. (1, 2) | 38. (1, 2, 4) | 39. (1, 4) |
| 40. (1, 2, 3) | 41. (1, 3, 4) | 42. (2, 3) |
| 43. (1, 4) | 44. (1, 3) | 45. (1, 3, 4) |
| 46. (1, 4) | 47. (2, 4) | 48. (1, 3) |

Linked Comprehension Type

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (4) | 2. (1) | 3. (2) | 4. (4) | 5. (3) |
| 6. (2) | 7. (4) | 8. (1) | 9. (3) | 10. (2) |
| 11. (3) | 12. (1) | 13. (2) | 14. (1) | 15. (1) |
| 16. (4) | 17. (3) | 18. (1) | 19. (4) | 20. (2) |
| 21. (1) | 22. (4) | 23. (3) | 24. (2) | 25. (4) |
| 26. (1) | | | | |

Matrix Match Type

Q.No.	a.	b.	c.	d.
1.	ii	iii, iv	i	iii
2.	ii	i, ii, iii	iv	iv
3.	iii	iv	i	ii

4.	iii	i	ii	iv
5.	iv	iii	ii	i
6.	iv	i	iii	ii
7.	iii	i	iv	ii
8.	iii	i	ii	iv
9.	iii	ii	iv	i
10.	ii	iii	i	iv
11.	ii-q	iii-p	iv-s	i-r

12. (2) 13. (1) 14. (1) 15. (3)

Numerical Value Type

1. (5) 2. (2) 3. (7) 4. (3) 5. (7)
 6. (7) 7. (8) 8. (0) 9. (7) 10. (7)
 11. (2) 12. (5)

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JEE Main

Single Correct Answer Type

1. (2) 2. (4) 3. (4) 4. (1) 5. (2)

JEE Advanced

1. (1) 2. (4)

Multiple Correct Answers Type

1. (2, 3, 4) 2. (1, 3, 4) 3. (1, 2, 4) 4. (2, 3) 5. (1, 3, 4)
 6. (2, 3)

Linked Comprehension Type

1. (3) 2. (1) 3. (1) 4. (1)

Matrix Match Type

1. (4)

Numerical Value Type

1. (0) 2. (5) 3. (7)

5

p-Block Group 18 Elements The Inert Family

OVERVIEW

- Group 18 elements comprise helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn).
- Group 18 elements are also known as inert gases, rare gases, noble gases, zerovalent elements or aerogens. However, the names inert gases and rare gases are misnomers.
- General electronic configuration of group 18 elements is $ns^2 np^6$, except He, whose electronic configuration is $1s^2$.
- Argon is the most abundant noble gas, about 1% by volume in air. It is nearly 30 times more abundant than CO_2 (0.03). In the universe, the order of abundance is $He > Ne > Ar > Kr > Xe$.

5. a. **Ionisation enthalpy:** $He > Ne > Ar > Kr > Xe > Rn$

b. **Melting point:** $Rn > Xe > Kr > Ar > Ne > He$

c. **Boiling point:** $Rn > Xe > Kr > Ar > Ne > He$

d. **Ease of liquefaction:** $Xe > Kr > Ar > Ne > He$

6. Helium can be diffused through rubber, glass or plastics.

7. Noble gases are monoatomic, colourless, odourless, tasteless, sparingly soluble in H_2O have low melting and boiling points due to weak van der Waals forces of attraction between the noble gas atoms.

8. True compounds of He, Ne and Ar are yet not discovered.

9. Most of the compounds of noble gases involve only fluorine and oxygen. This is due to the fact that any chemical reactivity shown by noble gases may be attributed to their tendency to lose electrons. For this reason, the combining atoms must be highly electronegative such as F (EN = 4.0) and O (EN = 3.5).

10. The only compound of Kr studied in detail is KrF_2 .

11. Xe in its compounds exhibits even oxidation states from +2 to +8.

Oxidation state	+2	+4	+6	+8
Compound	XeF_2	XeF_4	XeF_6	XeO_4

Xe also shows an oxidation state of +8 in perxenates, $[XeO_6]^{4-}$. Perxenates are strong oxidising agent and oxidises $Cl^- \longrightarrow Cl_2$, $H_2O \longrightarrow O_2$, $Mn^{2+} \longrightarrow MnO_4^-$ and $Ce^{3+} \longrightarrow Ce^{4+}$.

12. **Clathrates:** Noble gases form a number of combinations in which gases are trapped into the cavities of crystal

lattices of certain organic and inorganic compounds. These combinations are called cage compounds or clathrate compounds or enclosure. The crystal structure with cavities is called the 'Host' and the atom or molecule entrapped in it is called the 'Guest'. These are non-stoichiometric compounds, e.g., $Xe \cdot 6H_2O$, quinol clathrate. He and Ne do not form clathrate compounds as the size of the cavity is more than the size of the He or Ne atom.

13. Only He forms interstitial compounds with metals.

14. Solution of XeF_6 in HF is conducting due to formation of ions.

15. Discovery of noble gases:

Helium : Lockyer and Janssen

Neon : Ramsay and Travers

Argon : Lord Rayleigh and Ramsay

Krypton : Ramsay and Travers

Xenon : Ramsay and Travers

Radon : Dorn

16. On passing electric discharge through noble gases at low pressure (2 mmHg), the gas starts glowing with a characteristic colour. This phenomenon is used in glow signs also called neon signs. The colour also depends upon the pressure of the gas.

Colour of glow	Noble gas used	Pressure of the gas
Red	Neon	10–18 mm
White	Helium	3–4 mm
Light blue	Argon–Neon mixture + Hg vapours	10–20 mm

The colour can also be modified by the use of coloured glass for the discharged tube.

17. Neon is widely used in neon signs which are used for advertising purposes in the form of brilliant orange-red glow. This colour is changed by mixing argon and mercury vapours with neon to light blue. Since the light of neon signs has better penetrating power through fog and mist so these are used in beacon lights for safety of air navigations.

5.2 Inorganic Chemistry

18. Neon lamps are used in botanical gardens and the green houses as these stimulates growth and are effective in the formation of chlorophyll.
19. Argon is used for creating inert atmosphere in chemical reactions, welding and metallurgical operations and for filling in incandescent and fluorescent lamps. It is also used in filling Geiger-Counter tubes and thermionic tubes.
20. Krypton-85 clathrate provides a safe and useful source of β -radiations which are useful for measuring thickness of gauges.
21. Krypton and xenon are also used in gas-filled lamps. However, these gases are superior to argon but are very costly. A mixture of krypton and xenon is also used in some flash tubes for high speed photography. Radon is used in radioactive research and therapeutics and in the non-surgical treatment of cancer and other malignant growths.

5.1 GENERAL INTRODUCTION

The monoatomic gases, helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) constitute a separate family of elements known as **group 18 elements**. These elements have been called as inert gases, rare gases, aerogens, noble gases or group zero elements. The names inert gases and rare gases are misnomers. Initially these gases were referred as **inert gases** because of their chemical inertness. Their inertness was generally attributed to their very stable electronic configurations. With the discovery of large number of xenon compounds in 1962, it was shown that xenon is not inert and hence the name inert gases is a misnomer. These gases were also referred as **rare gases** because of their relatively uncommon existence on earth, but argon constitutes 0.9% by volume of the atmosphere and thus these gases are not rare.

Except Rn, all these gases occur in atmosphere and thus are sometimes referred to as **aerogens**. Nowadays, they are called **noble gases** so as to convey the impression that these gases do have some reactivity, just like noble metals such as gold and platinum, which are often reluctant to react and yet are not totally unreactive. These elements are also known as zerovalent elements as they show zero valency due to their chemical inertness. Consequently the group to which these elements belong is also known as zero group and these elements are known as **group zero elements**.

Julius Thomson justified the **position of noble gases in the periodic table by giving** argument that since there are highly electropositive elements (alkali metals) on extreme left and highly electronegative elements (halogens) on extreme right of the periodic table so there must be a group of elements which should form a bridge between highly electropositive and highly electronegative elements, which should neither be electropositive nor be electronegative, i.e. zero valency, that is why they are also known as **group zero elements**.

Lord Rayleigh and Sir William Ramsay were awarded the **noble prizes in 1904** for their discovery of noble gases.

Element	Sym-bol	Year of discovery	Name of discoverer	Origin of name
Helium	He	1895	Lockyer and Janssen	From the Greek word, 'helios' which means 'sun'
Neon	Ne	1898	Sir William Ramsay and Travers	From the Greek word, 'neos' which means 'new'
Argon	Ar	1894	Lord Rayleigh and Sir William Ramsay	From the Greek 'argos' which means 'inactive'
Krypton	Kr	1898	Sir William Ramsay and Travers	From the Greek word, 'kryptos' which means 'hidden'.
Xenon	Xe	1898	Sir William Ramsay and Travers	From the Greek word 'xenos' which means 'stranger'
Radon	Rn	1898	Friedrich Ernst Dorn	Named after the element 'radium'. Radon, was called nitron at first from the latin word 'nitens' meaning 'shining'

5.2 OCCURRENCE AND ABUNDANCE

On account of their inert nature, noble gases always occur in free state. Radon, being radioactive does not occur in free state as it decays rapidly. Its longest lived isotope has half life of less than four days. The chief sources of noble gases are:

Atmosphere: The total abundance of He, Ne, Ar, Kr and Xe in dry air is about 1% by volume of which Ar is the major component.

Table 5.1 Atomic and physical properties of group 18 elements

Property	Helium	Neon	Argon	Krypton	Xenon	Radon*
Symbol	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Atomic mass (g mol ⁻¹)	4.00	20.18	39.15	83.80	131.30	222.00
Electronic configuration	1s ²	[He] 2s ² 2p ⁶	[Ne] 3s ² 3p ⁶	[Ar] 3d ¹⁰ 4s ² 4p ⁶	[Kr] 4d ¹⁰ 5s ² 5p ⁶	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶
Atomic radii (pm)	120	160	190	200	220	—
Ionisation enthalpy (kJ mol ⁻¹)	2372	2080	1520	1351	1170	1037
Electron gain enthalpy (kJ mol ⁻¹)	48	116	96	96	77	68
Density (at STP) (g cm ⁻³)	1.8 × 10 ⁻⁴	9.0 × 10 ⁻⁴	1.8 × 10 ⁻³	3.7 × 10 ⁻³	5.9 × 10 ⁻³	9.7 × 10 ⁻³
Melting point (K)	—	24.6	83.8	115.9	161.3	202.0
Boiling point (K)	4.2	27.1	87.2	119.7	165.0	211.0
Enthalpy of vapourisation (kJ mol ⁻¹)	0.09	1.77	6.5	9.0	12.6	16.4
Abundance in atmospheric (% volume)	5.4 × 10 ⁻⁴	1.8 × 10 ⁻³	0.934	1.14 × 10 ⁻⁴	8.7 × 10 ⁻⁶	—

*Radioactive.

5.3 ATOMIC AND PHYSICAL PROPERTIES

Some of the atomic and physical constants of the noble gases have been summarised in Table 5.1.

5.3.1 MONOATOMIC NATURE

All the 18 group elements are colourless, odourless, monoatomic gases, as all the noble gases have stable ns^2np^6 valence shell electronic configuration, except He whose configuration is $1s^2$. Their monoatomic nature is supported by the following facts:

1. The ratio of their specific heat at constant pressure and constant volume, i.e. $C_p/C_v \approx 1.66$.
2. At STP, 22.4 L of each gas weighs equal to the atomic mass of the gas in grams.

Their monoatomic nature confirms their inert behaviour. They do not form diatomic molecules because they do not possess any unpaired electron. He has the usual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastic.

5.3.2 ATOMIC RADII

The atomic radii of the noble gases are the largest in their respective periods. The reason being in case of noble gases the radii is **van der Waals radii** due to instantaneous dipole-induced dipole interaction amongst the noble gas atoms; whereas in other groups it is covalent radii. In case of noble gases, covalent radii cannot be determined as they can be solidified at very low temperature only and at such low temperature X-ray crystallography cannot be performed.

Down the group (\downarrow), i.e. from He to Rn, the atomic radii increases primarily because at each successive step new shells are being added and the electron cloud is expanding.

Atomic radii: $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$

5.3.3 IONISATION ENTHALPY

The ionisation enthalpies of noble gases are the highest as compared to ionisation enthalpies of other members in the same period due to the stable electronic configurations.

Down the group (\downarrow), i.e. from the He to Rn, ionisation enthalpy decreases because of increase in atomic radii (size effect) and screening effect of the inner electrons.

Ionisation enthalpy: $\text{He} > \text{Ne} > \text{Ar} > \text{Kr} > \text{Xe} > \text{Rn}$

5.3.4 ELECTRON GAIN ENTHALPY

The electron gain enthalpy of noble gases is positive, as noble gases have completely filled subshells. Hence, the additional electron has to be placed in an orbital of next higher shell. Consequently, energy has to be supplied to add an additional electron and hence, the electron gain enthalpy of noble gases is positive.

Down the group (\downarrow), i.e. from He to Rn, as the size of the atom increases, electron gain enthalpies become less positive.

5.3.5 MELTING AND BOILING POINTS

The melting and boiling points of noble gases are extremely low in comparison to those substances of comparable atomic and molecular mass. This is because there is no strong interatomic forces. Only weak **van der Waals** forces operate which hold atoms together in liquid and solid state.

Down the group (\downarrow), i.e. their melting and boiling points increase due to increase in the magnitude of **van der Waals** forces of attraction with the increase in the atomic size. The very small difference in melting and boiling point indicates that solids are easily vapourised so that they remain gases at the temperature at which most of other elements are liquids or solids.

Helium has the lowest boiling point of any known substance. Gaseous He on cooling below 4.2 K condenses to a liquid known as Helium-I, which on cooling to 2.2 K at 1 atm pressure changes into a remarkable liquid known as Helium-II. Helium-II exhibits the following properties:

- High heat conductance, i.e. 600 times that of Cu at room temperature.
- Low viscosity i.e. 1/1000 th of H_2 gas. Thus it is virtually frictionless.
- It is also able to flow uphill.

5.3.6 ENTHALPY OF VAPOURISATION

It gives a measure of energy required to overcome the forces of attraction between noble gas atoms. The forces of attraction between the noble gas atoms are **van der Waals** forces which are very weak and arises due to instantaneous dipole-induced dipole.

Down the group (\downarrow), instantaneous dipole-induced dipole increases or polarisability increases, with increase in atomic size and therefore **van der Waals** forces increase. Hence enthalpy of vapourisation increases.

Enthalpy of vapourisation: $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$

5.3.7 EASE OF LIQUEFACTION

It is relatively difficult to liquefy noble gases due to weak **van der Waals** forces of attraction between the atoms.

It is only the weak **van der Waals** forces (London dispersion forces) which are responsible for the liquefaction of these gases.

Down the group (\downarrow), with the increase in atomic size, the magnitude of **van der Waals** forces of attraction increases and hence ease of liquefaction increases.

Ease of vapourisation: $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$

5.3.8 SOLUBILITY IN WATER

Noble gases have relatively high solubility in water, i.e., solubility of Ar in H_2O is greater than that of O_2 or N_2 .

Down the group (\downarrow), i.e. from He to Rn, solubility in water increases.

Noble gases are soluble in water due to **dipole-induced dipole interaction**. Water is a polar molecule. Due to dipole in H_2O , an induced dipole is created in noble gas atoms, due to distortion or polarisation of otherwise symmetrical electron cloud of noble gas atom (Figure 5.1).

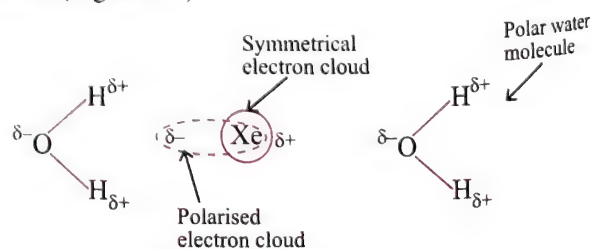


Fig. 5.1 Polarisation of Xe atom by H_2O molecule

Down the group (\downarrow), the atomic size increases and the attraction of the electron cloud to its nucleus decreases and this results in greater distortion of their electron cloud by the polarising water molecule. The magnitude of dipole-induced dipole interaction increases with the increasing size of the noble gases and consequently, their solubility in water increases down the group (\downarrow).

Solubility in water: $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$

5.4 CLATHRATE COMPOUNDS

Clathrate compounds are also known as cage compounds or inclusion compounds. According to Powell, in the clathrates, atoms or molecules (known as guests) of appropriate size are trapped in the cavities of crystal lattice of other compounds (known as host). Though the gases are trapped, they do not form true chemical bond. The only type of interaction in these compounds is the weak **van der Waals** forces. Clathrates are normally non-stoichiometric compounds. They are not true chemical compounds.

Essential conditions for clathrate compounds:

1. Presence of cavities of appropriate size in the crystal lattice of the host.
2. Size of the guest atom/molecule should be such as to fit in the cavities of the host without bringing any atoms closer together than which corresponds to **van der Waals** radii of the atom.

Stability of the clathrate compounds:

Clathrate compounds once formed are extremely stable because:

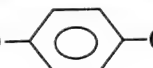
1. The guest molecule/atom fits tightly in the cavities of host molecule.
2. The guest molecules within the cages are at minimum potential energy.

Guest molecules can escape the host only when the forces holding the molecular cages together are overcome. This can be achieved by following two methods:

- a. By heating the clathrate compound.
- b. By dissolving the clathrate compound in suitable solvent such as alcohol.

Types of clathrates:

1. **Quinol clathrates:** When an aqueous solution of quinol

(i.e. 1,4-dihydroxy benzene, )

is crystallised under a pressure of 10–40 atm. of Ar, Kr or Xe, the noble gas atoms get trapped in the cavities of $\sim 4 \text{ \AA}$ in the β -quinol structure. The composition of these clathrates correspond to 3 quinol : 1 noble gas atom, though normally all cavities are not filled.

When the quinol clathrate is heated or dissolved in solvent, the hydrogen bonded arrangement of β -quinol breaks and noble gas escapes.

The smaller noble gases, He and Ne, do not form clathrate compounds because the noble gas atoms are small enough to escape through the cavities.

2. **Noble gas hydrates:** These are clathrate compounds but more commonly are referred to as noble gas hydrates. The noble gases Ar, Kr and Xe are trapped in the cavities formed when water is frozen under high pressure of gas. Their composition is approximately $6\text{H}_2\text{O} : 1$ noble gas atom. He and Ne do not form hydrates as they are too small as compared to the size of the cavity and thus escape through the cavities.

Uses:

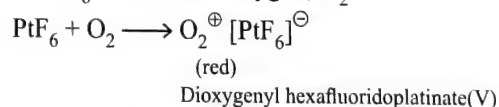
- a. Clathrate compounds provide a convenient means of storage and transportation of radioactive isotopes of Kr and Xe produced in nuclear reactors.
- b. Clathrates play an important role in the separation of noble gases. For example, neon can be separated from argon, krypton and xenon by forming clathrates with quinol because neon is the only gas that does not form such clathrates with quinol.
- c. Clathrates play an important role in some physiological actions, e.g., it is thought that the anaesthetic action of xenon is due to aqueous clathrate formation in physiologically strategic spots. When the anaesthetic is no longer administered the clathrates equilibrium is destroyed, the clathrates decompose and the consciousness returns.

5.5 INTERSTITIAL COMPOUNDS

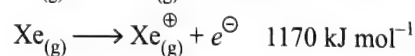
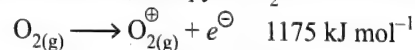
Interstitial compounds are formed when small atoms occupy the interstitial space of the metal lattice. Only He forms interstitial compounds since the atomic size of He is the smallest amongst the noble gases and matches the size of the interstices available in the lattice of most of the heavy metals.

5.6 CHEMISTRY OF NOBLE GAS COMPOUNDS

The first noble gas compound was made in 1962. **Bartlett** and **Lohman** had used highly oxidising compound platinum hexafluoride, PtF_6 to oxidise dioxygen, O_2 .

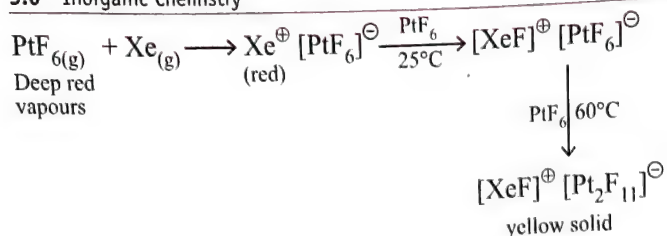


Since first ionisation enthalpy of O_2 and Xe are almost same,



it was predicted that Xe should also react with PtF_6 . It was experimentally shown that when deep red vapours of PtF_6 were mixed with equal volume of Xe, the gases combined immediately to give yellow solid. It was (incorrectly) thought that the product is $\text{Xe}^+[\text{PtF}_6]^-$ [Xenon hexafluoridoplatinate(V)]. The reaction has since been found to be more complicated, and the product is $[\text{XeF}]^+ [\text{Pt}_2\text{F}_{11}]^-$.

5.6 Inorganic Chemistry



Soon after this, it was found that Xe and F₂ react at 400°C to give colourless volatile solid XeF₄. Following this discovery, there was rapid extension of the chemistry of noble gases, in particular of xenon.

- Helium, neon and argon have much higher first ionisation enthalpy as compared to xenon, and hence similar compounds are not formed.
- Ionisation enthalpy of Kr is little lower and it forms KrF₂.
- Only compounds of radon identified by radiotracer technique is RnF₂.

Xenon forms stable compounds only with the most electronegative elements, i.e., F (EN = 4.0), O (EN = 3.5) or with highly electronegative groups such as OSF₅, OTF₅ that contain both oxygen and fluorine.

Of all the noble gases, Xe forms the largest number of compounds. This may be attributed to its low ionisation enthalpy.

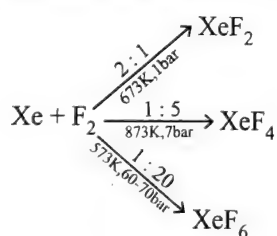
5.6.1 FLUORIDES OF XENON

Xenon reacts directly with fluorine to give binary fluorides:

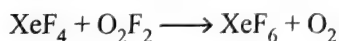
- Xenon difluoride, XeF₂
- Xenon tetrafluoride, XeF₄
- Xenon hexafluoride, XeF₆

Preparation:

- By heating Xe and F₂ at 400°C in a sealed nickel vessel. The products formed depends on Xe : F₂ ratio.



The method is not very good for XeF₂ because it readily reacts further under the experimental conditions to give XeF₄. XeF₆ can be prepared by the interaction of XeF₄ and O₂F₂ at 143K.



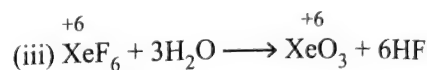
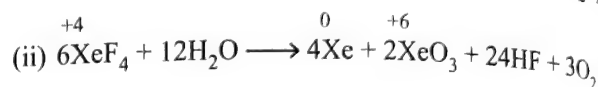
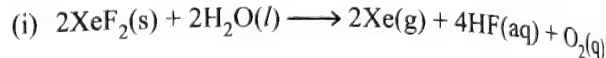
Properties:

- XeF₂, XeF₄ and XeF₆ are colourless crystalline solids and sublime readily at 298K. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water.
- Melting point:**

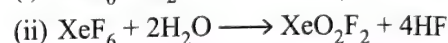
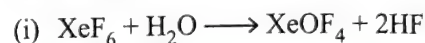
Xenon fluoride	XeF ₂	XeF ₄	XeF ₆
Melting point (°C)	140	117	49.5

Melting point decreases on moving from XeF₂ to XeF₄ to XeF₆, which is contrary to the usual trend. This is due to increase in polarity as the number of F-atoms bonded to Xe-atom increases. F^{δ+}—Xe^{δ+}—F^{δ-}. As the number of F-atoms bonded to Xe increases, there is more and more accumulation of +ve charge on Xe, which decreases the stability of the molecule.

Hydrolysis: XeF₂, XeF₄ and XeF₆.



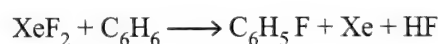
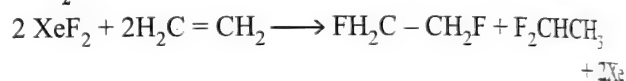
Partial hydrolysis of XeF₆:



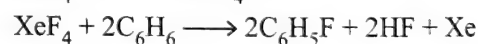
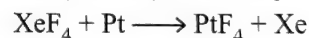
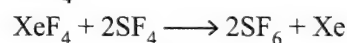
Note: Hydrolysis reaction is a non-redox reaction, since the hydrolysis are XeOF₄ and XeO₂F₄, where the O.S. of all elements remain same as it was in reacting state.

- As fluorinating agent:** All xenon fluorides act as strong fluorinating agents.

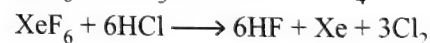
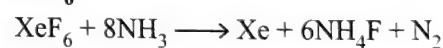
XeF₂:



XeF₄:



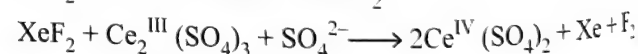
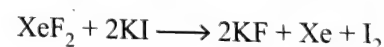
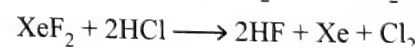
XeF₆:



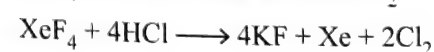
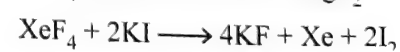
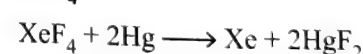
- As an oxidising agent:**

XeF₂:

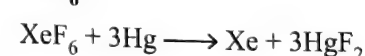
Oxidises Cl[⊖] → Cl₂, I[⊖] → I₂, etc.



XeF₄:



XeF₆:

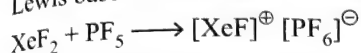


- Formation of addition compounds:**

XeF₂ acts as fluoride ion donor (Lewis base) and forms complexes with covalent pentafluorides including PF₅, AsF₅.

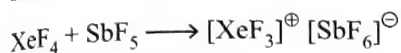
SbF₅ and the transition metal fluorides, NbF₅, TaF₅, RuF₅, OsF₅, RbF₅, IrF₅ and PtF₅ (Lewis acids). These are thought to have the following structure :

Lewis base + Lewis acid \longrightarrow Adduct



XeF₄ acts as fluoride ion donor (Lewis base) and forms few complexes with PF₅, AsF₅ and SbF₅.

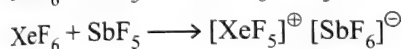
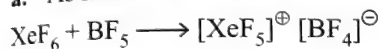
Lewis base + Lewis acid \longrightarrow Adduct



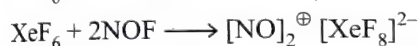
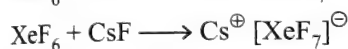
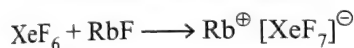
[XeF₃][⊕] has T-shaped structure.

XeF₆ acts both as fluoride ion donor (Lewis base) and as fluoride ion acceptor (Lewis acid).

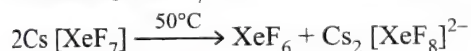
a. As fluoride ion donor



b. As fluoride ion acceptor



On heating, [XeF₇][⊖] decomposes as follows:



5.6.2 XENON OXIDES

Xenon forms two oxides: (i) xenon trioxide, XeO₃, and (ii) xenon tetraoxide, XeO₄.

1. Xenon trioxide, XeO₃

Preparation:

By complete hydrolysis of XeF₆ by atmospheric moisture (slow reaction)

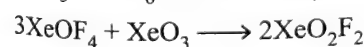
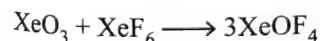


Properties:

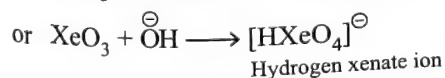
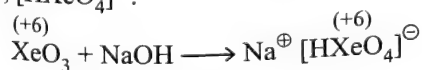
- White hyroscopic and highly explosive solid.
- Acts as strong oxidising agent. It oxidises Pu²⁺ to Pu⁴⁺ in the presence of H[⊕] ions.



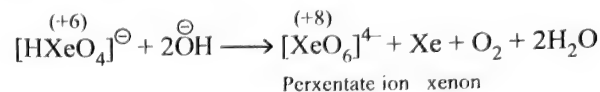
c. Reaction with XeF₆:



d. XeO₃ is soluble in water, but does not ionise. In solution, when pH > 10.5 (alkaline medium) it forms hydrogen xenate ion, [HXeO₄][⊖].

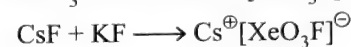
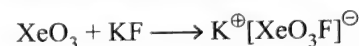


Hydrogen xenate ion, [HXeO₄][⊖] (oxidation state of Xe = +6) disproportionates slowly in solution to give perxenates, [XeO₆]⁴⁻ (oxidation state of Xe = +8) and xenon. (oxidation state of Xe = 0)

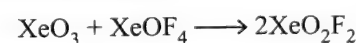


Solution of perxenates are yellow and act as powerful oxidising agents.

e. **With KF or CsF:** When a solution of XeO₃ is treated with KF or CsF, an oxo-fluoro salt, M[⊕][XeO₃F][⊖] is obtained.



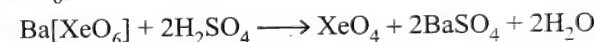
f. **With XeOF₄:**



2. Xenon tetraoxide, XeO₄

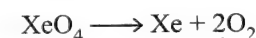
Preparation:

By the action of anhydrous or conc. H₂SO₄ on barium perxenate, Ba₂[XeO₆].

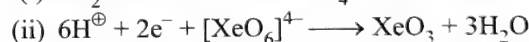
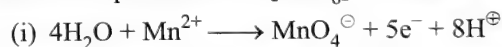


Properties:

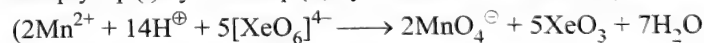
XeO₄ is not as stable as XeO₃ and decomposes to give Xe and O₂.



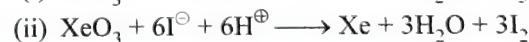
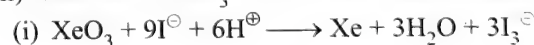
Reaction of perxenate ion [XeO₆]⁴⁻ with Mn²⁺ in acidic medium:



Multiply eq. (i) by 2 and eq. (ii) by 5 and add them. Net equation is:



(iii) Reaction of XeO₃ with I[⊖] ion in acidic medium



5.6.3 XENON OXYFLUORIDES

Xenon forms a number of oxyfluorides such as:

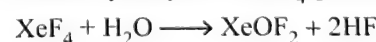
XeO₂F₂ Xenon dioxydifluoride

XeOF₄ Xenon oxytetrafluoride

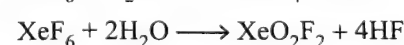
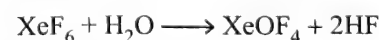
XeO₃F₂ Xenon trioxydifluoride

XeOF₂ Xenon oxydifluoride

i. Partial hydrolysis of XeF₄ gives XeOF₂

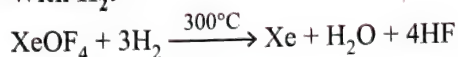


ii. Partial hydrolysis of XeF₆ gives oxyfluorides, XeOF₄ and XeO₂F₂.



Properties of XeOF₄:

- Clear, colourless mobile liquid which can be stored unchanged in Ni containers for long period.

b. With H_2 :

c. With silica:



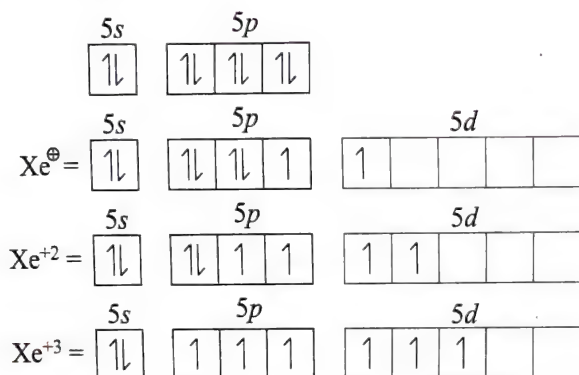
ILLUSTRATION 5.1

Explain:

- Why does Xe not form fluorides such as XeF , XeF_3 and XeF_5 ?
- Xe shows +8 O.S. e.g., in XeO_4 but XeF_8 is not formed. Why?
- Neon is used in safety devices for protecting electrical instruments?
- Neon is used in warning signal illumination.
- Why in deep sea diving a mixture of $(He + O_2)$ is used rather than $(Xe + N_2)$ why?

Sol.

a. $Xe = 5s^2 sp^6$



By unpairing of one period orbitals, two singly occupied orbitals comes into existence. Thus either two, four or six singly occupied orbitals can be formed instead of one, three or five singly occupied orbitals. Hence XeF , XeF_3 or XeF_5 are not formed.

- Eight small sized F atoms can not accomodate one large sized Xe atom. This is called steric effect or ligand crowding. Thus XeF_6 is not formed.
- This is due to the fact that Ne is capable of carrying extremely high current under high voltage.
- This is because Ne light is visible from long distances and even visible during fog and mist conditions.
- This is due to the fact that at high pressure N_2 gas is highly soluble in blood as compared to He and when the diver comes out of the sea a sudden change in pressure, causes degassing and releases bubbles of N_2 gas in blood. This causes painful condition called "bends" or caisson sickness. He is slightly soluble so risk of bends is reduced.

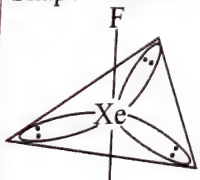
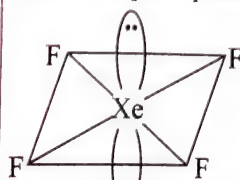
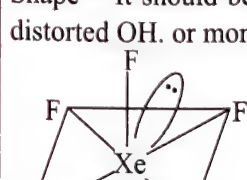
ILLUSTRATION 5.2

Give the important characteristics of Helium (II).

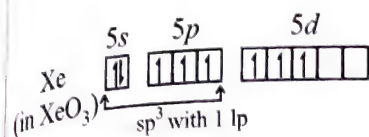
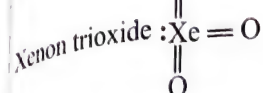
Sol. Liquid helium is unique in that it exists in two forms He I and He (liquid helium is obtained by Joule-Thomson expansion of the gas previously cooled to 15 K which is below the inversion temperature of He i.e., 35 K). The liquid helium I boils at 4.2 K and has normal liquid properties. On cooling He (I) to 2.19 K and 38 mm pressure, it changes to He (II) with abrupt changes in many physical properties such as density, dielectric constant and specific heat. He (II) is super fluid having so low energy that thermal motion of atoms do not take place, however, interatomic forces are also so weak that it does not occupy solid state. Thus He (II) is liquid with properties of gas. It has following characteristics:

- It has very high thermal conductance i.e., 800 times of copper.
- It has very low viscosity $\approx 1/100$ of H_2 gas.
- It has a very flat meniscus and very low surface tension and creeps over the surface of glass container.
- Its electrical resistance is zero i.e., it is super conducting liquid.
- He (II) has much lower entropy.

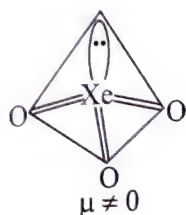
5.6.4 VALENCE BOND APPROACH FOR XENON COMPOUNDS

1	2	3																		
$:\ddot{X}eF_2$ Xenondifluoride <div style="text-align: center;"> Xe (in XeF_2) <table border="1" style="display: inline-table; vertical-align: middle;"> <tr> <td>5s</td> <td>5p</td> <td>5d</td> </tr> <tr> <td>$\uparrow\downarrow$</td> <td>$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$</td> <td>$\uparrow \quad \quad \quad$</td> </tr> </table> </div> <div style="text-align: center;"> $\xrightarrow{sp^3 d \text{ with 3 lp}}$ </div>	5s	5p	5d	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow \quad \quad \quad$	$:\ddot{X}eF_4$ Xenontetrafluoride <div style="text-align: center;"> Xe (in XeF_4) <table border="1" style="display: inline-table; vertical-align: middle;"> <tr> <td>5s</td> <td>5p</td> <td>5d</td> </tr> <tr> <td>$\uparrow\downarrow$</td> <td>$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$</td> <td>$\uparrow \uparrow \quad \quad$</td> </tr> </table> </div> <div style="text-align: center;"> $\xrightarrow{sp^3 d^2 \text{ with 2 lp}}$ </div>	5s	5p	5d	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow \uparrow \quad \quad$	$:\ddot{X}eF_6$ Xenonhexafluoride <div style="text-align: center;"> Xe (in XeF_6) <table border="1" style="display: inline-table; vertical-align: middle;"> <tr> <td>5s</td> <td>5p</td> <td>5d</td> </tr> <tr> <td>$\uparrow\downarrow$</td> <td>$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$</td> <td>$\uparrow \uparrow \uparrow \quad$</td> </tr> </table> </div> <div style="text-align: center;"> $\xrightarrow{sp^3 d^3 \text{ with 1 lp}}$ </div>	5s	5p	5d	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow \uparrow \uparrow \quad$
5s	5p	5d																		
$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow \quad \quad \quad$																		
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5s	5p	5d																		
$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow \uparrow \uparrow \quad$																		
SN = 2 bp + 3 lp = 5 $H = sp^3 d$, G = Trigonal bipyramidal Shape = Linear  $\mu = 0$	SN = 4 bp + 2 lp = 6 $H = sp^3 d^2$, G = Octahedral Shape = Square planar  $\mu = 0$	SN = 6 bp + 1 lp = 7 $H = sp^3 d^3$, G = Pentagonal bipyramidal Shape = It should be pentagonal pyramid. But it is distorted OH. or monocapped OH.  $\mu \neq 0$																		

4

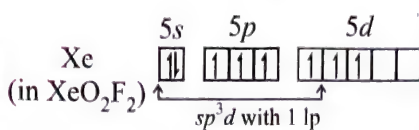
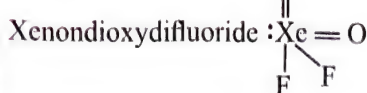


SN = 3 bp + 1 lp = 4
 $H = sp^3$, G = Tetrahedral
 Shape = Pyramidal

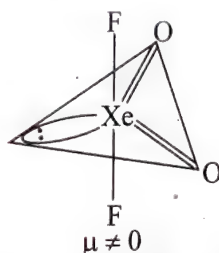


[3 ($p\pi-d\pi$) multiple bond]

5

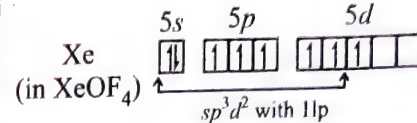
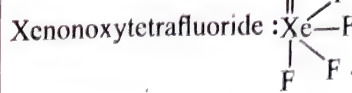


SN = 4 bp + 1 lp = 5, $H = sp^3d$
 G = T.b.p. See-saw shape saw horse
 or distorted/irregular. Tetrahedral

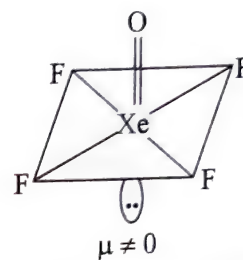


[2 ($p\pi-d\pi$) multiple bond]

6

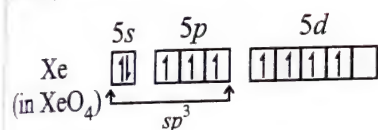


SN = 5 bp + 1 lp = 6, $H = sp^3d^2$
 G = Octahedral, Shape = Square pyramid

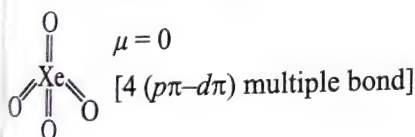


[one ($p\pi-d\pi$) multiple bond]

7.



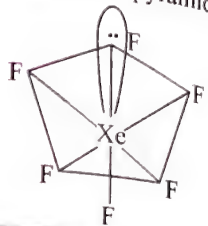

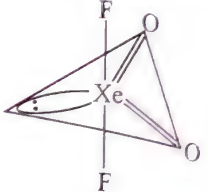
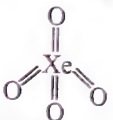
SN = 4 bp + 0 lp = 4, $H = sp^3$
 G = Tetrahedral, Shape = Tetrahedral



Note: Electrons used in π -bond formation are not included in the hybridised set of orbitals.

5.6.5 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY APPROACH FOR XENON COMPOUNDS

S.No.	Formula	No. of electron pairs	No. of bp	No. of lp	VSEPR explanation	Structure (shape)
1.	XeF_2 (Xenon difluoride)	$\frac{8+2}{2} = 5$	2	3	5 electron pairs—trigonal bipyramid geometry with 3 lp in equatorial positions	Linear
2.	XeF_4 (Xenon tetrafluoride)	$\frac{8+4}{2} = 6$	4	2	6 electron pairs—octahedral geometry, with 2 lp occupying axial position	Square planar

3.	XeF_6 (Xenon hexafluoride)	$\frac{8+6}{2} = 7$	6	1	7 electron pairs— pentagonal bipyramidal with 1 lp occupying the axial position OR distorted octahedral	Pentagonal pyramid 
4.	XeO_3 (Xenon trioxide)	$\frac{8+6}{2} = 7$	6	1	7 electron pairs — 3 bp involved in σ bond formation, 3 lp involved in π bond formation and 1 lp. Hence, it forms tetrahedral geometry Shape — pyramidal	Pyramidal 
5.	XeO_2F_2 (Xenon dioxy difluoride)	$\frac{8+4+2}{2} = 7$	6 ($4\sigma + 2\pi$)	1	4 bp involved in σ bond formation, 2 bp involved in π bond formation, 1 lp occupies equatorial position in pentagonal biypramidal geometry	See-saw 
6.	XeO_4 (Xenon tetraoxide)	$\frac{8+8}{2} = 8$	8 ($4\sigma + 4\pi$)	0	4 bp involved in σ bond formation, 4 bp involved in π bond formation resulting in tetrahedral geometry	Tetrahedral 

Note: Electrons involved in π bond formation must be subtracted before counting the number of electron pairs which determine the primary shape of the molecule.

5.7 USES OF NOBLE GASES

5.7.1 USES OF HELIUM (He)

- Helium has the lowest boiling point (4.2 K) of any liquid and hence it is used (i) in cryoscopy to obtain the very low temperatures required for superconductivity and lasers; (ii) as a cooling gas in one type of gas cooled nuclear reactor and (iii) as flow gas in gas-liquid chromatography.
- Helium is used in weather balloons and airships. Despite the fact that hydrogen gas has low density, lighter, cheaper and is more readily available than He, it is helium which is used in weather balloons and not hydrogen gas. The reason being that hydrogen gas is highly inflammable as compared to helium. As helium is heavier than H_2 , lifting power of helium is 92.6% as compared to that of H_2 .
- Due to high thermal conductivity, low viscosity and density, helium is used as flow gas in gas-liquid chromatography.
- It is used for filling electrical transformers.
- Both helium and nitrogen gas are inert, but it is helium which is used in preference to nitrogen to dilute oxygen in the gas cylinders used by divers in deep sea diving (mixture of $(\text{He} + \text{O}_2)$ is used rather than $(\text{He} + \text{N}_2)$). This is due to the fact that at high pressure, N_2 gas is highly soluble in blood as compared to He and when the diver comes out of the sea, a sudden change in pressure (a region of high pressure to low pressure), causes degassing and releases bubbles of nitrogen

gas in blood. This causes the painful condition called 'bends' or 'caisson sickness'. Helium is slightly soluble, so the risk of bends is not there or is reduced.

- Helium is used to provide inert atmosphere for the melting of easily oxidisable metals such as magnesium, aluminium, stainless steel etc.
- It is used to produce and sustain powerful conducting magnets, which are essential part of nuclear magnetic resonance (NMR) spectrometer and magnetic resonance imaging (MRI) systems, used for chemical diagnosis.
- Mixture of He and O_2 is used to treat asthma as it is very light and hence diffuses more rapidly than air through partly choked lung passages.
- Helium is suitable for low temperature gas thermometry because
 - It has low boiling point.
 - It has near ideal gas behaviour.

5.7.2 USES OF NEON (Ne)

- Neon emits a characteristic reddish orange glow when subjected to electric discharge at very low pressure. Hence a small amount of neon is used in neon discharge tubes and fluorescent bulbs for advertising display purposes.
- As the light of neon signs have a better penetrating power through fog and mist so these are used in beacon lights for safety of air navigation.

- Liquid Ne is used as cryogenic refrigerant as it has over 40 times the refrigerating capacity per unit volume than liquid He and three times that of liquid H₂.
- It is used to make gas lasers.
- Ne bulbs are used in botanical garden and in green houses.

5.7.3 USES OF ARGON (Ar)

- Provides inert atmosphere for metallurgical processes. This includes welding stainless steel, titanium, magnesium and aluminium.
- Used in the production of Ti (Kroll's process).
- Mixture of Ar and Hg vapours is used in fluorescent tubes.
- Argon along with N₂ gas is used in gas-filled electric lamps. It is superior to N₂ gas for filling electric lamps because
 - Thermal conductivity is Ar less than that of N₂.
 - Ar is more inert than N₂ gas, thus it does not endanger the life of the tungsten filament and thereby enhances the life of the lamp.
 - Being monoatomic, it does not dissociate even at high temperatures, so no heat is lost in breaking the atoms.
- It is used as a protective (non-reactive) atmosphere for growing crystals of Si and Ge.

5.7.4 USES OF KRYPTON (Kr)

- For filling luminous sign tubes and valves.
- Kr-85 is used in electronic tubes for voltage regulation and in leak testers.

5.7.5 USES OF XENON (Xe)

- Used in electric flash tubes for high speed photography.
- Xe-133 is used as a radioisotope.
- Perxenates are used in analytical chemistry as oxidising agents.

5.7.6 USES OF RADON (Rn)

- Used in radioactive research.
- Used in treatment of cancer and other malignant growths.
- Used for photographing the interiors of opaque materials i.e. locating defects in steel coatings and other metals and solids.

ILLUSTRATION 5.3

- Why are the elements of group 18 known as noble gases?
- Noble gases have very low boiling points. Why?
- Does the hydrolysis of XeF₆ lead to a redox reaction?

Sol.

- The elements present in group 18 have their valence shell orbitals completely filled and therefore react with a few elements only under certain conditions. Therefore, they are known as noble gases.

- Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence they have very low boiling points.

- No, the products of hydrolysis are XeOF₄ and XeO₂F₂, where the oxidation states of all the elements remain the same as it was in the reacting state.

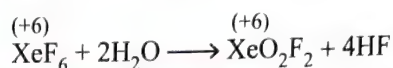
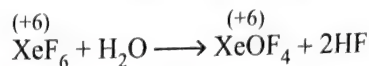


ILLUSTRATION 5.4

- What prompted Bartlett to the discovery of noble gas compounds?
- The majority of noble gas compounds are those of xenon. Give reason.
- No chemical compound of He is known. Why?

Sol.

- Since PtF₆ oxidises O₂ to O₂⁺, Bartlett thought that PtF₆ should also oxidise Xe to Xe⁺ because the ionisation enthalpies of O₂ (1175 kJ mol⁻¹) and Xe (1170 kJ mol⁻¹) are quite comparable.
- Except Rn, which is radioactive, Xe has the least ionisation enthalpy among group 18 elements and hence can be easily oxidised by strong oxidising agents like F₂ or O₂. That is why, majority of noble gas compounds are that of xenon.
- Helium does not form chemical compounds because:
 - Electronic configuration of He is 1s². The unpairing of electron cannot be done in He and hence it cannot form chemical compounds.
 - Ionisation enthalpy of He is very high.

ILLUSTRATION 5.5

Consider the following compounds in their solid state and find the value of expression. ($a + b - c$).

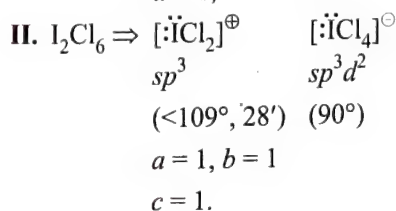
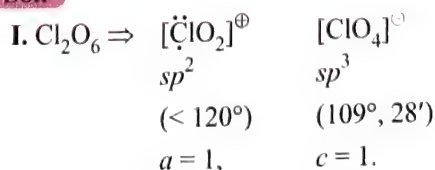
I. Cl₂O₆ II. I₂Cl₆ III. XeF₆

where a = Total number of compounds in which central atom of cationic or anionic part is sp^3 hybridised.

b = Total number of compounds having 90° bond angle either in cationic or anionic part.

c = Total number of compounds having 109°, 28' bond angle either in cationic or anionic part.

Sol.



Exercises

Single Correct Answer Type

Physical and Chemical Properties of Inert Gases

- Which of the following does not react with fluorine?
 - Kr
 - Ar
 - Xe
 - All of these
- Xenon directly combines with
 - oxygen
 - rubidium
 - fluorine
 - chlorine
- Xenon best reacts with
 - the most electropositive element
 - the most electronegative element
 - the hydrogen halides
 - non-metals
- Electron affinity for a noble gas is approximately equal to
 - that of halogens
 - zero
 - that of oxygen family
 - that of nitrogen family
- The gaseous mixture used by deep sea divers for respiration is
 - $N_2 + O_2$ mixture
 - $He + O_2$ mixture
 - $Ar + O_2$ mixture
 - neon + O_2 mixture
- The forces of cohesion in liquid helium are
 - covalent
 - ionic
 - van der Waals
 - metallic
- The lightest, non-inflammable gas is
 - H_2
 - He
 - N_2
 - Ar
- The inert gas present in atmosphere are
 - He and Ne
 - He, Ne and Ar
 - He, Ne, Ar and Kr
 - He, Ne, Ar, Kr and Xe.
- Inert gases such as helium behave like ideal gases over a wide range of temperature. However, they condense into the solid state at very low temperatures. It indicates that at very low temperature there is a
 - weak attractive force between the atoms
 - weak repulsive force between the atoms
 - strong attractive force between the atoms
 - strong repulsive force between the atoms
- The gas used for inflating the tyres of aeroplanes is
 - H_2
 - He
 - N_2
 - Ar
- A radioactive element X decays to give two inert gases. X is
 - ${}^{238}_{92}\text{U}$
 - ${}^{226}_{88}\text{Ra}$
 - ${}^{232}_{90}\text{Th}$
 - ${}^{227}_{89}\text{Ac}$
- Which gas is filled in electric bulbs/tubes?
 - O_2
 - N_2
 - Ar
 - He
- In colour discharge tubes, which is used?
 - Ne
 - Ar
 - Kr
 - He
- The ease of liquefaction of noble gases decreases in the order
 - $He > Ne > Ar > Kr > Xe$
 - $Xe > Kr > Ar > Ne > He$
 - $Kr > Xe > He > Ar > Ne$
 - $Ar > Kr > Xe > He > Ne$
- Compounds formed when the noble gases get entrapped in the cavities of crystal lattices of certain organic and inorganic compounds are known as
 - interstitial compounds
 - clathrates
 - hydrates
 - picrates
- Which compound is prepared by the following reaction?

$$Xe + 2F_2 \xrightarrow[673\text{ K, 5-6 atm}]{\text{Ni vessel}} \text{XeF}_2$$
 (1:5 volume ratio)
 - XeF_2
 - XeF_6
 - XeF_4
 - $XeOF_2$
- The two electrons in helium atom
 - occupy different shells
 - have different spins
 - have the same spins
 - occupy different subshells of the same subshell
- Helium gives a characteristic spectrum with
 - orange and red lines
 - orange lines
 - yellow lines
 - green lines
- The noble gas which behaves abnormally in liquid state is
 - Xe
 - Ne
 - He
 - Ar
- In order to prevent the hot metal filament from getting burnt, when the electric current is switched on, the bulb is filled with
 - CH_4
 - an inert gas
 - CO_2
 - Cl_2
- Radon is a noble gas. Its radioactivity is used in the treatment of
 - typhoid
 - cancer
 - cough and cold
 - thyroid
- Helium is used in gas balloons instead of hydrogen because
 - it is higher than H_2
 - it is non-combustible
 - it is more abundant than H_2
 - its linkage can be detected easily
- A helium atom on losing an electron becomes
 - α -particle

- (2) hydrogen atom
(3) positively charged helium ion
(4) negatively charged helium ion
24. Liquid flow from a higher to a lower level. Which of the following liquids can climb up the wall of the glass vessel in which it is placed?
(1) Alcohol (2) Liquid He
(3) Liquid N₂ (4) Water
25. Neon is extensively used in
(1) cold storage units
(2) organic compounds
(3) medicines
(4) coloured electric discharge lamps
26. The discovery of isotopes began with the experiments with
(1) Xe (2) Kr
(3) Ar (4) Ne
27. Which statement about noble gases is not correct?
(1) Xe forms XeF₆
(2) Ar is used in electric bulbs
(3) Kr is obtained during radioactive disintegration
(4) He has the lowest boiling point among all the noble gases
28. In solid argon, the atoms are held together by
(1) ionic bonds (2) hydrogen bonds
(3) van der Waals forces (4) hydrophobic forces
29. The van der Waals forces are the greatest in
(1) neon (2) argon
(3) krypton (4) xenon
30. Electronegativity of an inert gas is
(1) high (2) low
(3) negative (4) zero
31. Which has the same electronic configuration as of inert gas?
(1) Ag³⁺ (2) Cu²⁺
(3) Pb⁴⁺ (4) Ti⁴⁺
32. Which noble gas is not found in atmosphere?
(1) Rn (2) Kr
(3) Ne (4) Ar
33. Which noble gas is more soluble in water?
(1) He (2) Ar
(3) Ne (4) Xe
34. Which noble gas has highest and least polarisability respectively?
(1) He, Xe (2) Ne, Kr
(3) Kr, Ne (4) Xe, He
35. Asthma patients use a mixture of for respiration.
(1) O₂ and H₂ (2) O₂ and He
(3) O₂ and Ar (4) O₂ and Ne
36. The solubility of noble gases in water shows the order:
(1) He > Ar > Kr > Ne > Xe (2) He > Ne > Ar > Kr > Xe
(3) Xe > Kr > Ar > Ne > He (4) None of the above
37. Which of the following cannot be formed?
(1) He²⁺ (2) He⁺
(3) He (4) He₂
38. Which statement regarding He is incorrect?
(1) It is used in gas cooled nuclear reactor.
(2) It is used as a cryogenic agent for carrying out experiment at low temperature.
(3) It is used to produce and sustain powerful superconducting magnets.
(4) It is used to fill gas balloons instead of H₂ because it is lighter and non-combustible.
39. The idea that prompted Bartlett to prepare first ever compound of noble gases was
(1) Low bond dissociation enthalpy of F-F in F₂ molecule
(2) High bond energy of Xe-F
(3) Ionisation enthalpies of O₂ and Xe are almost same
(4) None of the above
40. Noble gases are also known as aerogens because
(1) They occur in air
(2) They are rarely found in atmosphere
(3) They are most rarely found in atmosphere
(4) None of the above
41. Helium-oxygen mixture is used by deep sea divers in preference to nitrogen-oxygen mixture because
(1) Nitrogen is much less soluble in blood than helium
(2) Helium is much less soluble in blood than nitrogen
(3) Nitrogen is highly soluble in water
(4) Due to high pressure deep under the sea nitrogen and oxygen react to give poisonous nitric oxide.
42. Hydrolysis of XeF₄ and CaCN₂ gives respectively:
(1) XeO₃ and CaCO₃ (2) XeOF₃ and CaCN₂
(3) XeO₂ and CaCN₂ (4) XeOF₂ and CaCO₃
43. Helium gives a characteristic spectrum with:
(1) Orange and red lines (2) Yellow lines
(3) Orange lines (4) Green lines
44. Which of the following noble gas does not form clathrate compound?
(1) Kr (2) Xe
(3) Ne (4) Ar
45. Which of the following is not true about helium?
(1) It can form clathrate compounds
(2) It can diffuse through rubber and plastic material
(3) It has the highest first ionization energy
(4) It has the lowest boiling point
46. Which compound is prepared by the following reaction?
- $$\text{Xe} + \text{F}_2 \xrightarrow[673 \text{ K}]{\text{Ni}}$$
- (2 : 1) volume ratio
(1) XeF₆ (2) XeF₂
(3) XeF₄ (4) None of these

47. In the clathrates of xenon with water, the nature of bonding between xenon and water molecule is:
- (1) Dipole-induced dipole interaction
 - (2) Hydrogen bonding
 - (3) Coordinate
 - (4) Covalent

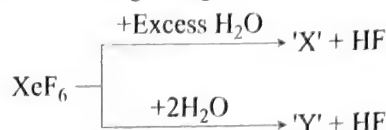
Compounds of Inert Gases

48. Which species is not known?
- (1) XeF_6
 - (2) XeF_4
 - (3) XeO_3
 - (4) KrF_6
49. The fluoride which does not exist is
- (1) CF_4
 - (2) SF_6
 - (3) HeF_4
 - (4) XeF_4
50. The non-existent species is
- (1) XeF_5
 - (2) BrF_5
 - (3) SbF_5
 - (4) PF_5
51. Geometry and hybridisation of Xe in XeOF_4 molecule is
- (1) square planar, sp^3d^2
 - (2) square pyramidal, sp^3d^2
 - (3) tetrahedral, sp^3
 - (4) none of the above
52. XeF_4 exists as under ordinary atmospheric conditions.
- (1) solid
 - (2) liquid
 - (3) gas
 - (4) none of these
53. The idea which prompted Bartlett to prepare first ever compound of noble gas was
- (1) high bond energy of Xe-F
 - (2) low bond energy of F-F in F_2
 - (3) ionisation energies of O_2 and xenon were almost similar
 - (4) none of the above
54. What are the products formed in the reaction of xenon hexafluoride with silicon dioxide?
- (1) $\text{XeSiO}_4 + \text{HF}$
 - (2) $\text{XeF}_2 + \text{SiF}_4$
 - (3) $\text{XeOF}_4 + \text{SiF}_4$
 - (4) $\text{XeO}_3 + \text{SiF}_2$
55. XeF_6 on complete hydrolysis gives
- (1) XeO_3
 - (2) XeO
 - (3) XeO_2
 - (4) Xe
56. Xenon tetrafluoride has hybridisation and structure as
- (1) sp^3 tetrahedral
 - (2) sp^3d^2 square planar
 - (3) sp^3d^2 pyramidal
 - (4) sp^3d^3 octahedral
57. In the clathrates of xenon with water, the nature of bonding between xenon and water molecule is
- (1) covalent
 - (2) hydrogen bonding
 - (3) coordinate
 - (4) dipole-induced dipole
58. Out of (i) XeO_3 (ii) XeOF_4 and (iii) XeF_6 , the molecules having same number of lone pairs on Xe are
- (1) (i) and (ii) only
 - (2) (i) and (iii) only
 - (3) (ii) and (iii) only
 - (4) (i), (ii) and (iii)
59. Which is planar molecule?
- (1) XeO_4
 - (2) XeF_4
 - (3) XeOF_4
 - (4) XeO_2F_2

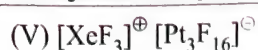
60. Which of the following is an explosive compound?

- (1) XeO_3
- (2) XeF_2
- (3) XeOF_2
- (4) XeOF_4

61. Incorrect statement regarding following reactions is:



- (1) XeF_6 can undergo partial hydrolysis
 - (2) Both are example of non-redox reaction
 - (3) 'Y' is an oxyacid of xenon
 - (4) 'X' is explosive
62. XeF_6 dissolves in anhydrous HF to give a good conducting solution which contains:
- (1) HXeF_6^+ and F^- ions
 - (2) HF_2^- and XeF_5^+ ions
 - (3) H^+ and XeF_7^- ion
 - (4) None of these
63. $\text{MF} + \text{XeF}_4 \longrightarrow \text{'A'} \text{ (M}^+ = \text{Alkali metal cation)}$
The state of hybridisation of the central atom 'A' and shape of the species are:
- (1) sp^3d^3 , distorted octahedral
 - (2) sp^3d , TBP
 - (3) sp^3d^3 , pentagonal planar
 - (4) No compound formed at all
64. The formation of $\text{O}_2^+ [\text{PF}_6]^-$ is the basis for the formation of xenon fluorides. This is because:
- (1) O_2 and Xe have comparable electronegativities
 - (2) O_2 and Xe have comparable ionization energies
 - (3) Both O_2 and Xe are gases
 - (4) O_2 and Xe have comparable sizes
65. Consider the following properties of the noble gases.
- (I) They readily form compounds which are colourless.
 - (II) They readily generally do not form ionic compounds.
 - (III) Xenon has variable oxidation states in its compound.
 - (IV) The smaller He and Ne do not form clathrate compound
- (1) I, II, III
 - (2) II, III, IV
 - (3) I, III, IV
 - (4) All
66. When a solution of XeO_3 is treated with metal fluoride, the product obtained is
- (1) $\text{M}^+ [\text{XeO}_6\text{F}]^-$
 - (2) $\text{M}^+ [\text{XeO}_3\text{F}]^-$
 - (3) $\text{M}^+ [\text{XeO}_2\text{F}_2]^-$
 - (4) None of these
67. Xenon tetra-fluoride, XeF_4 is
- (1) See-saw shape and acts as a fluoride donor with AsF_5
 - (2) Square planar and acts as fluoride donor with NaF
 - (3) Square planar and acts as a fluoride donor with PF_5
 - (4) Tetrahedral and acts as a fluoride donor with SbF_5
68. $\text{Xe(g)} + \text{PtF}_6\text{(g)} \longrightarrow \text{A} \xrightarrow[25^\circ\text{C}]{\text{PtF}_6} \text{B} \xrightarrow[60^\circ\text{C}]{\text{PtF}_6} \text{C}$
The products are:
- (I) $\text{Xe}^+ [\text{PtF}_6]^-$
 - (II) $[\text{XeF}]^+ [\text{PtF}_{11}]^-$
 - (III) $[\text{XeF}]^+ [\text{Pt}_3\text{F}_{16}]^-$
 - (IV) $[\text{XeF}_2]^+ [\text{Pt}_2\text{F}_{11}]^-$



(1) I, VI, II

(3) VI, II, III



(2) I, II, III

(4) I, IV, V

69. Which one of the following correctly represents Xe—F bond length?

(1) $\text{XeF}_4 > \text{XeF}_2 > \text{XeF}_6$ (2) $\text{XeF}_2 > \text{XeF}_4 > \text{XeF}_6$ (3) $\text{XeF}_6 > \text{XeF}_4 > \text{XeF}_2$

(4) None of these

70. SbF_5 reacts with XeF_4 to form an adduct. The shapes of cation and anion in the adduct are respectively:

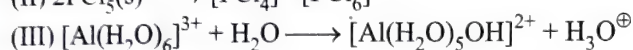
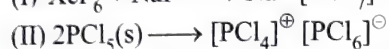
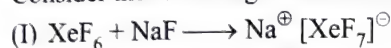
(1) Square pyramidal, octahedral

(2) T-shaped, octahedral

(3) Square planar, trigonal bipyramidal

(4) Square planar, octahedral

71. Consider the following transformations:



Possible transformations are:

(1) I, II, III

(2) I, III

(3) I, II

(4) II, III

72. Which of the following is an uncommon hydrolysis product of XeF_2 and XeF_4 ?

(1) HF

(2) O_2

(3) Xe

(4) XeO_3

73. Out of (i) XeO_3 , (ii) XeO_2F_2 and (iii) XeO_4 , the molecules having same number of lone pairs are

(1) (i) and (ii)

(2) (ii) and (iii)

(3) (i) and (iii)

(4) None of these



The products [X] and [Y] in unbalanced reaction are:

(1) H_2XeO_4 and Xe(2) $[\text{XeO}_6]^{4-}$ and XeO_3 (3) XeO_3 and Xe(4) $[\text{XeO}_6]^{4-}$ and Xe

75. XeF_2 and XeF_6 are separately hydrolyzed then:

(1) XeF_6 gives O_2 and XeF_2 does not

(2) Neither of them gives HF

(3) XeF_2 alone gives O_2 (4) Both give out O_2

76. Which of the following compounds has the same number of lone pairs as in I_3^-

(1) XeF_2 (2) XeF_4 (3) XeO_3 (4) XeO_4

77. The noble gases can be separated by

(1) Adsorption and desorption on activated hydrogen

(2) Passing them through suitable solution

(3) Electrolysis of their fluorides.

(4) Adsorption and desorption on charcoal

78. Which factor is responsible for the increase in boiling points from He to Xe?

(1) Increase in polarisability (2) Decrease in polarisability

(3) Decrease in I.E.

(4) Mono-atomic nature

79. The compound that cannot be formed by Xe is:

(1) XeO_2F_2 (2) XeF_4 (3) XeCl_4 (4) XeO_3

Multiple Correct Answers Type

Physical and Chemical Properties

1. The noble gases which do not form any clathrate

(1) He

(2) Ne

(3) Ar

(4) Kr

2. Which of the following noble gases do not react with fluorine?

(1) Kr

(2) Xe

(3) He

(4) Ne

3. The noble gases found dissolved in some spring water are

(1) He

(2) Ne

(3) Kr

(4) Ar

4. Boiling point and melting point of noble gases are in the order

(1) $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$ (2) $\text{He} > \text{Ne} > \text{Kr} > \text{Ar} > \text{Xe}$ (3) $\text{He} < \text{Kr} < \text{Ne} < \text{Ar} < \text{Xe}$ (4) $\text{He} > \text{Kr} > \text{Ne} > \text{Ar} > \text{Xe}$

5. Which of the noble gases has its ionisation enthalpy close to that of molecular oxygen?

(1) Ar

(2) Xe

(3) Kr

(4) Rn

6. The following observations are shown by

1. It is used for filling airships and balloon for meteorological purposes because of its power equal to 92% that of H_2 .

2. With O_2 , it is used by deep sea divers for respiration and also used in the treatment of respiratory diseases like asthma.

3. Providing inert atmosphere in the welding of metals or alloys that are easily oxidised.

4. Used for inflating the tyre of big aeroplanes because of lightness.

5. Used in cryoscopic experiment.

(1) Ne

(2) Ar

(3) He

(4) Kr

7. He is added to the oxygen supply used by sea divers because

(1) it is less soluble in blood than N_2 at high pressure(2) it is lighter than N_2 (3) it is readily miscible with O_2 (4) it is less poisonous than N_2

8. Which of the following statements are not correct?

(1) Ar is not used in electric bulbs.

(2) Kr is obtained during radioactive decay

(3) Boiling point of helium is the lowest among all noble gases.

(4) Xe forms XeOF_4

9. The coloured discharge tubes for advertisement mainly contains

- (1) Xe (2) Ne
(3) He (4) Ar

10. Xenon reacts with

- (1) the most electropositive element
(2) the most EN element
(3) the hydrogen halide
(4) Non-metals

11. $Xe > Kr > Ar > Ne > He$. This order represents

- (1) ease of vapourization (2) enthalpy of vapourisation
(3) ionisation enthalpy (4) solubility in water.

12. Which of the following statements are true?

- (1) Xenon fluorides are not reactive.
(2) Hydrolysis of XeF_6 is a redox reaction.
(3) Ionisation enthalpy of molecular oxygen is very close to that of xenon.
(4) Only type of interactions between particles of noble gases are due to weak dispersion forces.

13. Select the correct order.

- (1) $XeF_6 < XeF_4 < XeF_2$ – (Xe—F bond length)
(2) $XeF_6 > XeF_4 > XeF_2$ – (melting point)
(3) $He < Ne < Ar < Kr < Xe$ – (boiling point)
(4) $He > Ar > Kr > Ne > Xe$ – (abundance in air)

14. Helium is used as flow gas in gas liquid chromatography due to

- (1) high thermal conductivity (2) low density
(3) low viscosity (4) low thermal conductivity

Compounds of Inert Gases

15. XeF_4 on reaction with H_2 gives

- (1) Xe (2) HF
(3) XeF_2 (4) XeF_6

16. Which of the following compounds cannot be prepared by direct reaction between the constituent elements?

- (1) XeF (2) XeO_3
(3) XeF_4 (4) XeO_2F_2

17. Which amongst the following statements are correct?

- (1) XeF_4 and SbF_5 combine to form salt.
(2) He and Ne do not form clathrates.
(3) He has highest boiling point in its group.
(4) He diffuses through rubber.

18. Which of the possible following fluorides of Xenon is impossible?

- (1) XeF_2 (2) XeF_4
(3) XeF_6 (4) XeF_3

19. Xenon fluorides are colourless and at room temperature are:

- (1) Solid (2) Liquid
(3) Gases (4) Superfluid

20. Discovery of noble gas compounds were the basis of formation of an ionic solid, dioxxygenyl hexafluoridoplatinate (V), $O_2^+[PtF_6]^-$, when O_2 reacts with PtF_6 . This experiment was carried out by

- (1) Bartlett and Lohman (2) Ramsay
(3) Dawar (4) Fischer-Ringe

21. Which one of the following does not exist?

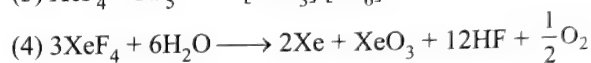
- (1) XeF_2 (2) XeF_4
(3) ArF_2 (4) XeF_6

22. When deep red PtF_6 vapour was mixed with Xe at room temperature to produce a yellow ionic solid. The product is

- (1) $Xe^+[PtF_6]^-$ (2) $[XeF^+][Pt_2F_{11}]^-$
(3) Both (a) and (b) (4) None

23. Which of the following reactions of xenon compounds is incorrect?

- (1) $XeF_2 + HF \longrightarrow H[XeF_3]$
(2) $XeF_6 + RbF \longrightarrow [XeF_5][RbF_2]$
(3) $XeF_4 + PF_5 \longrightarrow [XeF_3][PF_6]$



24. Which of the following statements are incorrect?

- (1) $XeOF_4$ can be stored in Ni containers for long period.
(2) Xenon trioxide on treatment with xenon oxytetra-fluoride
(3) Partial hydrolysis of XeF_6 gives oxy-fluorides.
(4) When $pH > 10.5$ xenon trioxide in solution forms hydrogen xenate ion.

25. XeF_6 cannot be stored in glass vessel because silica (SiO_2) in glass reacts with XeF_6 to form

- (1) $[XeF_5]^+$ (2) XeO_3
(3) XeO_2F_2 (4) $XeOF_4$

26. Which among the following statements is/are correct?

- (1) He has lowest boiling point in its group.
(2) He diffuses through rubber and polyvinyl chloride.
(3) He and Ne do not form clathrate.
(4) XeF_4 and SbF_5 combine to form salt.

27. Select the correct statement(s) regarding the fluorides of xenon.

- (1) All three fluorides are volatile, readily subliming at room temperature (298 K).
(2) XeF_4 and XeF_6 can act as fluoride ion acceptors as well as fluoride ion donors.
(3) All three fluorides are powerful oxidizing agents.
(4) All three fluorides are decomposed by water, XeF_2 slowly and, XeF_4 , and XeF_6 rapidly.

28. Select the correct statements.

- (1) XeO_3 reacts with KI in acidic medium to give I_3^- and I_2
(2) XeO_3 disproportionate in basic medium
(3) Perxenate $[XeO_6]^{4-}$ disproportionate in basic medium.
(4) XeF_6 reacts with glass

Linked Comprehension Type

Paragraph 1

Noble gases have completely filled valence shell i.e. ns^2np^6 , except He ($1s^2$). Noble gases are monoatomic under normal conditions.

Low boiling points of the lighter noble gases are due to weak van der Waals forces between the atoms and absence of any interatomic interactions. Xe reacts with F_2 to give a series of fluorides namely XeF_2 , XeF_4 , XeF_6 . XeF_6 on complete hydrolysis gives XeO_3 .

1. Structure of XeF_4 is

- (1) Linear (2) Square planar
(3) Tetrahedral (4) Pyramidal

2. Oxidation state of Xe in XeF_2 is

- (1) +2 (2) +4
(3) +6 (4) +8

3. Argon is used in arc welding due to its

- (1) Flammability
(2) High calorific value
(3) Low reactivity with metal
(4) Lower the melting point of metal

4. XeF_4 and XeF_6 are expected to be

- (1) Reducing (2) Oxidising
(3) Inert (4) Basic

Matrix Match Type

This section contains questions each with two columns-I and II. Match the items given in column I with that in column II.

Column I (compound)		Column II (hybridisation of Xe)	
a.	XeF_2	i.	sp^3d^3
b.	XeF_4	ii.	sp^3d^2
c.	XeF_6	iii.	sp^3
d.	XeO_3	iv.	sp^3d
e.	XeO_2F_2	v.	sp^3d^2
f.	XeO_4	iv.	sp

Column I		Column II	
a.	XeF_2	i.	Square pyramidal
b.	$XeOF_4$	ii.	Linear
c.	XeF_4	iii.	Distorted octahedral
d.	XeF_6	iv.	Square planar
e.	XeO_4	v.	Pyramidal
f.	XeO_3	iv.	Tetrahedral

Column I		Column II	
a.	Neon	i.	Cryogenic
b.	Helium	ii.	Ionisation energy comparable to O_2
c.	Xenon	iii.	Advertising sign
d.	Argon	iv.	Provides inert atmosphere in metallurgy
e.	Radon	v.	Cancer treatment
f.	Krypton	vi.	High speed photography

4. Match the following:

Compound		Hybridisation		Geometry and shape	
a.	XeF_2	i.	sp^3	1.	Linear
b.	XeF_4	ii.	sp^3d^3	2.	Square planar
c.	XeF_6	iii.	sp^3d^2	3.	Expected pentagonal pyramid but distorted octahedral
d.	XeO_3	iv.	sp^3d^2	4.	Expected tetrahedron but pyramidal

5. Match the following:

Compound		Hybridisation		Geometry and shape	
a.	$XeOF_2$	i.	sp^3d	1.	Expected trigonal but T-shaped
b.	$XeOF_4$	ii.	sp^3d	2.	Expected octahedron but square pyramidal
c.	XeO_2F_2	iii.	sp^3d^2	3.	Trigonal bipyramid with one position occupied
d.	XeO_3F_2	iv.	sp^3d	4.	Trigonal bipyramid
e.	$Ba_2[XeO_6]^{4+}$	vi.	sp^3d^2	5.	Octahedron

Column I		Column II	
a.	XeF_6	i.	Basic gas evolves on heating
b.	$(NH_4)_2S$	ii.	Oxidising agent
c.	$H_2PO_3^-$	iii.	Disproportionation in basic medium/heating
d.	Cl_2	iv.	Reacts with water/hydrolysis
e.	NO_2		

7. Match the items given in Column I with that in Column II and III

Column I		Column II		Column III	
Reactions		Products		Characteristics	
a.	Partial hydrolysis of XeF_6 . $\text{XeF}_6 + \text{H}_2\text{O} \longrightarrow \dots + 2\text{HF}$	i.	XeF_2	p.	sp^3d^2 , square pyramid
b.	Partial hydrolysis of XeF_6 . $\text{XeF}_6 + 2\text{H}_2\text{O} \longrightarrow \dots + 4\text{HF}$	ii.	XeOF_4	q.	sp^3d , linear
c.	Complete hydrolysis of XeF_6 . $\text{XeF}_6 + 3\text{H}_2\text{O} \longrightarrow \dots + 6\text{HF}$	iii.	XeO_2F_2	r.	sp^3d , folded square
d.	Complete hydrolysis of XeF_4 . $6\text{XeF}_4 + 12\text{H}_2\text{O} \longrightarrow 4\text{Xe} + 24\text{HF} + 3\text{O}_2 + \dots$	iv.	XeO_3	s.	sp^3 , pyramidal.
e.	$\text{Xe}(\text{in excess}) + \text{F}_2(\text{g}) \xrightarrow[1 \text{ bar}]{2:1, 6.73\text{K}}$				

For Q. 8 to Q. 11

Answer the questions given below by appropriately matching the information given in three Column of the following table.

Column I		Column II		Column III	
Noble gases		Characteristics (I)		Characteristics (II)	
a.	$3s^2 3p^6$	i.	Highest ease of liquefaction	p.	Along with O_2 , gas is used for deep sea diving
b.	$5s^2 5p^6$	ii.	High thermal conductivity, low viscosity and density.	q.	Forms clathrate compounds
c.	$1s^2$	iii.	Its electronic configuration is: $[\text{He}]2s^2 2p^6$	r.	React with PtF_6 to give orange red ionic solid
d.	$2s^2 2p^6$	iv.	Its name is derived from Greek word which means 'inactive'	s.	It is used in discharge tubes and fluorescent bulbs for advertising display purposes

8. For helium, CORRECT combination is:

- (1) c—ii—p (2) c—ii—s
(3) d—iii—s (4) d—iii—p

9. For neon, CORRECT combination is:

- (1) a—iv—q (2) a—iv—r
(3) d—iii—s (4) d—i—s

10. For argon, CORRECT combination is:

- (1) a—iv—q (2) a—iv—r
(3) d—iii—s (4) d—i—s

11. For Xenon, CORRECT combination is:

- (1) b—i—q (2) b—i—q,r
(3) b—ii—q (4) b—ii—q,r

Numerical Value Type

- What is the oxidation number of Xe in XeOF_2 ?
- What is the total number of electrons present in the last orbit of Argon?
- What is the percentage of Argon in air?
- What is the total number of unpaired electrons in inert gas?
- What is the total number of lone pair of electrons present in Xe in XeF_2 ?
- What is the oxidation state of Xe in XeF_6 ?
- How many $d\pi-p\pi$ bonds are there in XeO_4 ?

Archives

JEE MAIN

Single Correct Answer Type

1. The mineral cleveite on heating gives
(1) He (2) Xe
(3) Ar (4) Ra

(AIEEE 2006)

2. Which of the following reactions is an example of redox reaction?

- (1) $\text{XeF}_4 + \text{O}_2\text{F}_2 \longrightarrow \text{XeF}_6 + \text{O}_2$
(2) $\text{XeF}_2 + \text{PF}_5 \longrightarrow [\text{XeF}]^+ \text{PF}_6^-$
(3) $\text{XeF}_6 + \text{H}_2\text{O} \longrightarrow \text{XeOF}_4 + 2\text{HF}$
(4) $\text{XeF}_6 + 2\text{H}_2\text{O} \longrightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$

(JEE Main 2017)

3. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are:

- (1) ClO^- and ClO_3^- (2) ClO_2^- and ClO_3^-
 (3) Cl^- and ClO^- (4) Cl^- and ClO_2^-

(JEE Main 2017)

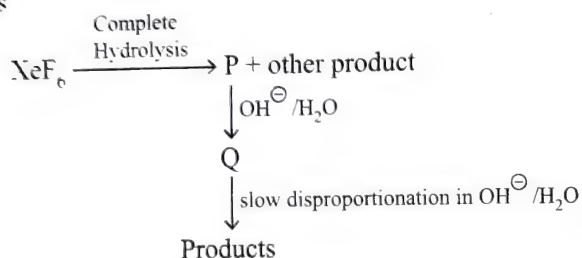
JEE ADVANCED**Single Correct Answer Type**

1. The shape of XeO_2F_2 molecule is

- (1) Trigonal bipyramidal (2) Square planar
 (3) Tetrahedral (4) See-saw

(IIT-JEE 2012)

2. Under ambient conditions, the total number of gases released products in the final step of the reaction scheme shown below is



- (1) 0 (2) 1
 (3) 2 (4) 3

(JEE Advanced 2014)

3. Which one has the highest boiling point?

- (1) He (2) Ne
 (3) Kr (4) Xe

(JEE Advanced 2015)

Linked Comprehension Type

The noble gases have closed-shell electronic configuration and are monatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to the weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6. XeF_4 reacts violently with water to give XeO_3 . The compounds of xenon

exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell

1. Argon is used in arc welding because of its
 (1) low reactivity with metals.
 (2) ability to lower the melting point of metals.
 (3) flammability
 (4) high calorific value

2. The structure of XeO_3 is

- (1) linear (2) planar
 (3) pyramidal (4) T-shaped

3. XeF_4 and XeF_6 are expected to be

- (1) oxidising (2) reducing
 (3) unreactive (4) strongly basic

(IIT-JEE 2007)

Matrix Match Type

1. All the compounds listed in column I react with water. Match the result of the respective reactions with the appropriate options listed in column II.

Column I		Column II	
a.	$(\text{CH}_3)_2\text{SiCl}_2$	p.	Hydrogen halide formation
b.	XeF_4	q.	Redox reaction
c.	Cl_2	r.	Reacts with glass
d.	VCl_5	s.	Polymerisation
		t.	O_2 formation

(IIT-JEE 2010)

Numerical Value Type

1. A list of species having the formula XZ_4 is given below.

XeF_4 , SF_4 , SiF_4 , BF_4^- , $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{FeCl}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$.

Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

(JEE Advanced 2014)

2. The total number of lone pairs of electrons in N_2O_3 is

(JEE Advanced 2013)

Answers Key**EXERCISES****Single Correct Answer Type**

1. (2) 2. (3) 3. (2) 4. (2) 5. (2)
 6. (3) 7. (4) 8. (4) 9. (2) 10. (2)
 11. (2) 12. (3) 13. (2) 14. (2) 15. (2)
 16. (3) 17. (2) 18. (3) 19. (3) 20. (2)
 21. (2) 22. (2) 23. (3) 24. (2) 25. (4)
 26. (4) 27. (3) 28. (3) 29. (4) 30. (4)

31. (4) 32. (1) 33. (4) 34. (4) 35. (2)
 36. (3) 37. (4) 38. (4) 39. (3) 40. (1)
 41. (2) 42. (1) 43. (2) 44. (3) 45. (1)
 46. (2) 47. (1) 48. (4) 49. (3) 50. (1)
 51. (2) 52. (1) 53. (3) 54. (3) 55. (1)
 56. (2) 57. (4) 58. (4) 59. (2) 60. (1)
 61. (3) 62. (2) 63. (3) 64. (2) 65. (2)
 66. (2) 67. (3) 68. (1) 69. (2) 70. (2)
 71. (1) 72. (4) 73. (1) 74. (4) 75. (3)
 76. (1) 77. (4) 78. (1) 79. (3)

Multiple Correct Answers Type

1. (1, 2) 2. (3, 4) 3. (1, 4)
 4. (1) 5. (2) 6. (3)
 7. (1) 8. (1, 2) 9. (2)
 10. (2) 11. (1, 2, 4) 12. (3, 4)
 13. (1, 3) 14. (1, 2, 3) 15. (1, 2)
 16. (2, 4) 17. (1, 2, 4) 18. (4)
 19. (1) 20. (1) 21. (3)
 22. (3) 23. (1, 2) 24. (2)
 25. (2, 3, 4) 26. (1, 2, 3, 4) 27. (1, 2, 3, 4)
 28. (1, 4)

Linked Comprehension Type

1. (2) 2. (1) 3. (3) 4. (2)

Matrix Match Type

Q.No.	a	b	c	d	e	f
1.	iv	v	i	iii	iv	iii
2.	ii	i	iv	iii	vi	v
3.	iii	i	ii	iv	vi	v
4.	iv, 1	iii, 2	ii, 3	i, 4		
5.	iv, 1	iii, 2	ii, 3	i, 4	v, 5	
6.	ii, iv	i, iv	i, iii, iv	ii, iii, iv	ii, iii, iv	
7.	ii, p	iii, r	iv, s	iv, s	i, q	

8. (1) 9. (3) 10. (1) 11. (2)

Numerical Value Type

1. (4) 2. (8) 3. (1) 4. (0) 5. (3)
 6. (6) 7. (4)

ARCHIVES**JEE Main****Single Correct Answer Type**

1. (1) 2. (1) 3. (3)

JEE Advanced**Single Correct Answer Type**

1. (4) 2. (3) 3. (4)

Linked Comprehension Type

1. (1) 2. (3) 3. (1)

Matrix Match Type

1. (a) p, s (b) p, q (c) p, q, t (d) p

Numerical Value Type

1. (4) 2. (8)

6

d- and f-Block Elements

OVERVIEW

d-Block transition elements (T.E.):

- The *d*-block elements are called transition elements (T.E.). General electronic configuration is $(n-1)d^{1-10}ns^{1-2}$.
- Zn, Cd and Hg are called non-typical T.E. They have completely filled $(n-1)d$ orbitals, their atoms are not expected to form covalent bonding amongst themselves, hence they have relatively low melting and boiling points (b. pt.) than the other *d*-block elements.
- T.E. lie between electropositive (E.P.) *s*-block elements and electronegative (E.N.) *p*-block elements in the periodic table.
- In representative elements (*s* and *p* blocks) the valence electrons are present only in the outermost shell while in transition elements, the valence electrons are present in the outermost shell as well as *d*-orbitals of penultimate shell.
- All transition elements are *d*-block elements, but all *d*-block elements are not transition elements.
- The transition elements show both covalent and metallic bonding amongst their atoms.
- The *d*-block elements do not form ionic compounds so readily as the alkali and alkaline earth metals.
- Unlike the *s*-block elements, *d*-block elements have a tendency to form covalent compounds under certain conditions.
- Generally, compounds with lower oxidation state (O.S.) are ionic while the compounds with higher O.S. are covalent.
- All the T.E. have simple *ccp*, *hcp* or *bcc* lattice characteristic of true metals. They have high tensile strength, thermal, electrical conductivity and lustre.
- Melting point (m. pt.) of 3*d* series rises to maximum and fall as the atomic number (*Z*) increases except in Mn where m. pt. is minimum. Melting point of T.E. except Zn, Cd and Hg are above 900°C. Mn and Tc (technetium) have abnormally low m.pt. W (tungsten) has highest melting point (3410°C) amongst T.E.
- In a series, the atomic radii first decrease up to the middle of the series and then become constant and at the end of the series show a slight increase.
- The atomic radii increase down the group (↓) from 3*d* T.E. series to be 4*d* T.E. series, but the atomic radii of 4*d* and 5*d* T.E. series are almost same, due to the consequence of lanthanoid contraction, e.g., size of Zr ≈ size of Hf and size of Nb ≈ size of Ta.
- Ability to show several O.S. is due to comparable energy of $(n-1)d$ and *ns* orbitals. Sc, Y, La and Ac do not show variable valency.
- Many transition elements exhibit oxidation states which differ from each other only by one unit (e.g., Fe(II) and Fe(III)). This is in marked contrast to the *s*-block elements which exhibit only the group valency and the *p*-block elements which exhibit either the maximum group valency or valency less by two units due to inert pair effect.
- In general, the minimum oxidation state shown by any transition element is equal to the number of *ns*-electrons. For the first five members of each transition series, the highest oxidation state shown, in general, is equal to the sum of *ns* and $(n-1)d$ -electrons. For the remaining five elements, the maximum oxidation state is not related to their electronic configuration. The highest oxidation state shown by any transition element is + 8.
- The + 2 oxidation state becomes more stable while the -3 state becomes less stable from left to right in the periodic table.
- Some transition elements also show an oxidation state of zero in their compounds e.g., $[\text{Ni}(\text{CO})_4]$ and $[\text{Fe}(\text{CO})_5]$.
- In general, for the first four elements of a transition series, higher oxidation states are more stable than lower oxidation states. For the next five elements lower oxidation states are more stable than higher oxidation state e.g., Cr(III) is more stable than Cr(II) but Mn(II) is more stable than Mn(III).
- IE_2 of the transition series increases almost regularly with increase in atomic number. However the value for Cr and Cu are sufficiently higher than those of their neighbours. This is due to stable configuration of Cr^{3+} ($3d^5$ exactly half-filled) and Cu^{+} ($3d^{10}$ completely filled).
- The 5*d*-transition elements (Group 4–12) possess higher ionisation energies than 3*d* and 4*d*-transition elements due to the greater effective nuclear charge (Z_{eff}) in 5*d*-transition elements. This is due to imperfect shielding effect of 4*d*-electrons in 5*d* transition elements.
- $E^{\ominus}_{\text{M}^{2+}/\text{M}}$ values are more negative than $E^{\ominus}_{2\text{H}^{\oplus}/\text{H}}$ values. (except Cu). These metals (except Cu) evolve $\text{H}_{2(\text{g})}$ and

hence are oxidised easily when reacted with acid solutions. $E^{\ominus}_{\text{Cu}^{2+}/\text{Cu}}$ is highest (+ 0.34) in first transition series and does not liberate $\text{H}_{2(\text{g})}$ from acids.

23. Cr is unreactive although high negative $E^{\ominus}_{\text{Cr}^{2+}/\text{Cr}}$ value due to the formation of non-reactive invisible layer of Cr_2O_3 .

24. $E^{\ominus}_{\text{M}^{3+}/\text{M}^{2+}}$ of Co and Ni is exceptionally high positive value due to high (negative) hydration enthalpy.

25. They show good catalytic properties due to the presence of a number of electrons and their capability to form unstable intermediate compound which readily decomposes yielding product and catalyst.

26. Most of the compounds of T.E. are coloured in solid or in aqueous solution. This is due to $d \leftarrow d\gamma$ or $t_{2g} \leftarrow e_g$ transition in the visible range and exhibit complementary colour.

27. The T.E. ions having completely filled d -orbitals and completely empty d -orbitals are colourless e.g., Zn^{2+} , Cd^{2+} and Hg^{2+} , Cu^+ , Ag^+ and Sc^{3+} and Ti^{4+} .

28. T.E. and their compounds show paramagnetic behaviour due to the presence of unpaired electron. It is due to spin angular momentum and orbital angular momentum.

For 1st T.E. series, the contribution of the orbital angular moment is neglected. Therefore, the magnetic moment is determined by the number of unpaired electrons and is calculated by spin only formula.

$$\mu = \sqrt{n(n+2)} \text{ BM (Bohr magneton)}$$

$$1 \text{ BM} = \frac{eh}{4\pi mc} = 9.27 \times 10^{-24} \text{ Am}^2 \text{ or J T}^{-1}$$

29. T.E. ions have ability to form complexes due to small size, high nuclear charge and a number of vacant d -orbitals of comparable energy.

30. They have the ability to form interstitial compounds in which small non-metals occupy the interstitial sites and form bonds with them. These are known as hydrides, carbides, borides, nitrides respectively and hence have high m. pt. than those of pure metals. They are chemically inert, hard and rigid, e.g. steel and cast iron are interstitial compounds of Fe and C. They form nonstoichiometric compounds and have indefinite compositions e.g., $\text{Fe}_{0.94}\text{O}_4$, $\text{TiH}_{1.7}$, $\text{VH}_{0.56}$ etc.

The malleability and ductility of metal decrease and tenacity increases.

31. They form alloys due to similarity in their atomic sizes, and the atoms of one element can substitute the atoms of other metals in their crystal lattice. Then m.pt. of alloys are generally high, but the m.pt. of alloys are lower than their pure metals. Alloys of Hg are called amalgams.

32. Many transition metal compounds are isomorphous e.g., $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ because of almost equal ionic sizes of these metals.

33. Lightest transition metal is Sc (density 3.1 g cm^{-3}) and heaviest and densest transition element is Os.

34. When the metals like Fe, Co and Ni are placed in magnetic field, their magnetic domains are turned so that all of them point in the same direction giving rise to a large magnetic effect. Such substance are known as ferromagnetic.

35. Cu^{\oplus} with d^{10} configuration should be stable but actually Cu^{2+} ion is more stable than Cu^{\oplus} ion because of increased hydration.

36. Mn shows maximum state of +7 in KMnO_4 .

37. Highest oxidation state shown by any transition element is + 8 (Ru in $4d$ -series and Os in $5d$ -series).

38. Mercury is the only liquid metal at room temperature.

39. Zinc metal is brittle and hard at room temperature.

40. Most abundant and most widely used transition metal is iron.

41. Mo is used in X-ray tube, Ta in analytic weights and instruments used in surgery of veins.

42. TiCl_4 and TiO_2 are used in smoke screens.

43. Platinum is inert (or noble metal) but it dissolves in aqua regia due to the formation of H_2PtCl_6 .

44. Mercurous ions exist as dimer Hg_2^{2+} and not as Hg^{\oplus} and this explains its diamagnetic nature.

45. The first synthetic element is Tc ($Z = 43$) (technetium man-made artificial).

46. Alnico which is an alloy of Al (12%), Co (50%), Ni (20%) and rest iron is used to make permanent magnets.

f-Block elements or inner transition elements or rare earth elements:

Lanthanoids

1. General electronic configuration: $(n-2)f(n-1)d^0-1 ns^2$

2. f -Block elements are divided into two series:

(i) Lanthanoids (Ln) and (ii) Actinoids

3. In the electronic configuration of Ln ($4f^{1-14}, 5d^0-1, 6s^2$), electron can shift between f - and d -orbitals depending upon the stability of electronic configuration.

4. Lanthanoids having electronic configuration of $4f^2$ and $4f^8$ are not known.

5. There is gradual steady decrease in atomic/ionic radii in lanthanoid series from La to Lu and La^{3+} to Lu^{3+} due to lanthanoid contraction.

6. Due to lanthanoid contraction, pairs of elements such as Zr/Hf, Nb/Ta and Mo/W are almost identical in size. Due to the same reason, sizes of $5d$ elements are very similar to those of $4d$ elements and they resemble closely. Thus their separation is difficult. However, they can be separated by (i) ion exchange method using zeolite catalyst and (ii) valency change methods.

7. The magnetic moment of f -block elements is calculated by considering spin as well as orbital quantum contribution.

$$\text{i.e., } \mu_{(S+L)} = \sqrt{4S(S+1) + L(L+1)} \text{ BM}$$

8. Sizes of Ln^{3+} decrease (from La^{3+} to Lu^{3+}), the covalent character increases and hence basic strength decreases.

9. Their most predominant and stable O.S. is +3, they also exist in +2 and +4 O.S., but they have a tendency to revert back to +3 O.S.

10. They show limited number of O.S. because there is a large energy gap between $4f$ and $5d$ subshells.

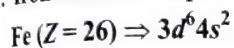
11. They are used in the production of alloy steel known as **mischmetal**, which is used in making Mg-based alloy, known as **pyrophoric alloys**.

Actinoids

1. General electronic configuration: $5f^{1-14}, 6d^{0-1} 7s^2$.
2. Actinides having electronic configuration of $5f^1, 5f^5$ and $5f^8$ are not known.
3. Like lanthanoids, there is gradual steady decrease in atomic/ionic radii in actinoids series from Ac to Lr. This is called **actinoid contraction**. This contraction is greater from element to element in this series due to poor shielding by $5f$ -electrons.
4. Besides +3 O.S., they show higher state of +4, +5, +6 and +7 also. This is due to very small gap between $5f, 6d$ and $7s$ subshell.
5. They are more basic, have greater tendency towards complex formation and they are radioactive.

Compounds of metals:

I. Iron and its compounds



It is a reactive metal and do not occur in free state. In combined state it occurs in the form of ores.

Some important ores are:

- i. Haematite (Fe_2O_3)
- ii. Magnetite (Fe_3O_4)
- iii. Limonite ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)
- iv. Iron pyrites (FeS_2)
- v. Copper pyrites (CuFeS_2)

The following compounds of iron have been discussed in the chapter.

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Green vitriol), Fe_2O_3 , FeO , Fe_3O_4 , FeS , FeCl_3 , and $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

Some important points of Fe and its compounds:

1. Fe^{2+} is green and Fe^{3+} is yellow.
2. Fe^{3+} is powerful oxidising agent than Fe^{2+} ion.
3. FeCl_3 is used as styptic to stop bleeding from a cut.
4. Iron is rendered passive by conc. HNO_3 and other oxidising agents like $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , chloric acid, chromic acid, silver nitrate etc. A specimen of passive iron can be rendered active by scratching the film mechanically or chemically (e.g., immersing in conc. alkali solution, heating in reducing atmosphere of H, or CO).
5. Slag is formed only by ferrous oxide (FeO), ferric oxide (Fe_2O_3) does not form a slag.
6. Iron carbide or cementite is Fe_3C .
7. FeSO_4 is used in manufacture of blue black ink.
8. Kipp's base is $\text{FeS} + \text{H}_2\text{SO}_4$.
9. Mohr's salt is resistant to atmospheric oxidation.
10. Copper dissolves in an aqueous solution of FeCl_3 .

II. Copper ($\text{Cu} = 29$) $\Rightarrow 3d^{10} 4s^1$

Important ores of copper are as follows:

- i. Copper pyrites (chalcopyrite): CuFeS_2 or $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$
- ii. Cuprite (Ruby copper): Cu_2O

iii. Copper glance: Cu_2S

iv. Malachite: $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$

v. Azurite: $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$

The following compounds of Cu have been discussed in the chapter: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Blue vitriol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CuO , Cu_2O

Some important points of Cu and its compounds:

1. Copper is the second most useful metal (the first being iron).
2. Verdigris is $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{Cu}(\text{OH})_2$ i.e., basic copper acetate and is used as a green pigment in paints.
3. Matte contains $\text{Cu}_2\text{S} + \text{FeS}$.
4. Schweitzer's reagent contains copper and is used for dissolving cellulose in the manufacture of artificial silk or rayon.
5. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is called blue vitriol or 'Nila thotha'.
6. CuF_2 is an ionic solid.
7. CuCl_2 and CuBr_2 are covalent and exist as polymers.
8. CuFeS_2 is called Fool's gold.
9. If an arc is struck between the two copper rod dipped in water, a colloidal solution of copper is obtained.
10. $\text{Cu}(\text{NO}_3)_2$ is monomeric and $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ is dimeric in vapour state.
11. Blister copper contains 96–98% copper with small amounts of Ag and Au as impurity.
12. Bordeaux mixture (CuSO_4 solution + lime) is used as fungicide.
13. $\text{CuSO}_{4(\text{aq})}$ reacts only with I^\ominus ion but does not react with Cl^\ominus , Br^\ominus and F^\ominus ions.
14. With $[\text{Fe}(\text{CN})_6]^{4-}$, Cu^{2+} gives reddish brown ppt. of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$.

III. Zinc ($\text{Zn} = 30$) $\Rightarrow 3d^{10} 4s^2$

Important ores of zinc are as follows:

- i. Zincite (red zinc ore): ZnO
- ii. Franklinite: $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$
- iii. Zinc blende: ZnS
- iv. Calamine (zinc spar): ZnCO_3

Some important points of Zn and its compounds:

1. Impure zinc is known as spelter.
2. The process of depositing a thin layer of zinc on metals like iron is called **Galvanisation**. It prevents rusting of iron.
3. Rinman's green, a green pigment is $\text{ZnO} \cdot \text{CoO}$.
4. Zinc dissolves in alkali forming sodium zincate and hydrogen.
$$\text{Zn} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$$
5. Zinc dust is used as a reducing agent.
6. ZnS is used in preparing X-ray screens.
7. Zinc sulphide containing trace of radium salt (1 part in 10 million parts) is used as luminous paint for watch dials.
8. Lithopone, a white paint, is $\text{ZnS} + \text{BaSO}_4$.
9. ZnO is called philosopher's wool.

IV. Silver Ag ($Z = 47$) $\Rightarrow 4d^{10}5s^1$

Silver is found in the free (native) as well as combined state. Native silver usually occurs and associated with copper and gold.

Important ores are as follows:

- i. Argentite (silver glance): Ag_2S
- ii. Horn silver: AgCl
- iii. Ruby silver (pyrargyrite): $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$

Lead and copper ores are generally contaminated with silver. Argentiferous galena (lead sulphide containing argentite as impurity) contains 0.01–0.1% silver.

The following compounds of Ag have been discussed in the chapter:

AgNO_3 (Lunar caustic), AgBr , Ag_2O , $\text{Ag}_2\text{S}_2\text{O}_3$.

Some important points of Ag and its compounds:

1. Silver leaves are used in Ayurvedic and Yunani medicine.
2. Molten silver dissolves 20 times its volume of oxygen.
3. Silver amalgam is used in silvering of mirrors and in filling teeth.
4. Silver metal is best conductor of heat and electricity.
5. Sterling silver (80% Ag, 20% Cu) is used in making Jewellery.
6. Silver is not attacked by aqua regia but it reacts with conc. H_2SO_4 and conc. HNO_3 .
7. Silver reacts with sulphur or H_2S forming black Ag_2S hence silver cutlery is tarnished black by food rich in sulphur (mustard and egg yolk).
8. **Spitting of silver:** Molten silver absorbs oxygen which is given off on cooling causing violet spurting. This is called spitting of silver.
9. Silvering of mirror is based on reduction of ammoniacal silver nitrate solution by neutral solution of tartarate or glucose in cold.
10. AgNO_3 is called Lunar caustic.
11. All silver halides except AgF are insoluble in water.
12. AgI is insoluble in NH_4OH but AgCl is soluble in NH_4OH due to formation of $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$.
13. AgBr is most sensitive to photoreduction. AgI is not so sensitive to light. Both AgBr and AgI are used in photography.
14. Ag_2O is a brown coloured solid insoluble in water.
15. Silver nitrate is used for preparing marking inks and hair dyes.

V. Gold Au ($Z = 79$) $\Rightarrow 5d^{10}6s^1$

Gold is found in the native (free) as well as in combined state. The following compounds of Au have been discussed in the chapter:

AuCl_3 and Au_2S

Some important ores are as follows:

- i. Bismuthaurite: BiAu_2

- ii. Sylvanite $(\text{Ag} \cdot \text{Au})\text{Te}_2$
- iii. Calverite: AuTe_2

Some important points of Au and its compound:

1. Ag, Cu and Au like coinage metals and their reactivity decrease in the order $\text{Cu} > \text{Ag} > \text{Au}$.
2. Gold is soluble in mercury.
3. The nobility of metals increases with increase in atomic number from Cu to Au.
4. Gold is considered to be the king of metals.
5. Fulminating gold: It is $\text{Au}(\text{NH}_2) = \text{NH}$ or $\text{N}_2\text{H}_3 \cdot \text{Au}$.
6. Gold and silver are highly malleable and ductile.
7. Purity of gold is expressed in fineness or carat. Pure gold is 24 carats.
8. Generally small quantity of other metals like copper are added to gold to make it hard.
9. Molten gold has a shining green lustre.
10. Purple of Cassius is a colloidal solution of gold.

VI. Mercury Hg ($Z = 80$) $\Rightarrow 5d^{10}6s^2$

Important ore is Cinnabar: HgS

The following compounds of Hg have been discussed in the chapter:

Hg_2Cl_2 (calomel), HgCl_2 (corrosive sublimate) and HgI_2 .

1. Mercuric thiocyanate is used for making **Pharaoh's serpents**. For this purpose, it is mixed with a little gum made into pellets, which when dried and ignited, yield a serpent like voluminous ash.
2. Mercuric salts are more stable than mercurous salts.
3. Mercury forms alloys (called Amalgam) with all metals except iron and platinum. Hence, mercury is transported in iron containers.
4. When a little of mercury is poured into an AgNO_3 solution, a tree like growth of silver amalgam is produced. This is called **mercury tree**.
5. Alkaline solution of K_2HgI_4 is called **Nessler's reagent** and gives brown precipitate $[\text{HgI} \cdot \text{HgO} \cdot \text{NH}_2]$ or iodide of millon's base with ammonia.
6. Mercuric chloride or **corrosive sublimate** is HgCl_2 . It is poisonous and best antidote for it is white of an egg.
7. HgS is used as a cosmetic under the name **Vermillion** and in Ayurvedic medicine **Makardhwaja**. HgS produced by either direct combination or by precipitation by H_2S is black in colour. This black HgS on sublimation gives the bright red coloured product used as vermilion or as Makardhwaja.
8. Mercury vapour is invisible and has no shining appearance as the liquid metal has.
9. Calomel, Hg_2Cl_2 is used for making standard calomel electrode, used as a reference electrode.
10. Mercury is the liquid metal at room temperature.

6.1 INTRODUCTION

Transition elements are elements of *d*-block and consist of elements lying between *s* and *p*-blocks starting from 4th period onwards.

The *d*-block of the periodic table contains the elements of the group 3–12 in which *d*-orbitals are progressively filled in each of the four long periods. In these elements the differentiating electron (i.e. the last electron) enters the penultimate subshell i.e. $(n-1)d$ subshell.

The **general electronic configuration** of these metals is $(n-1)d^{1-10}ns^{1-2}$. The properties of these elements are transitional between those of *s* and *p*-block elements. All these elements are metal.

Strictly speaking, a transition element is defined as one which has incompletely filled *d*-orbitals in its ground state or any one of its stable oxidation state (O.S.).

Thus, Zn, Cd and Hg of group 12 having full d^{10} configuration

in their ground state as well as in their common oxidation states (e.g., Zn^{2+} , Cd^{2+} and Hg^{2+}) are not regarded as transition metals. However, being the end members of three transition series, their chemistry is studied along with the chemistry of the transition metals.

In modern terminology, the **general electronic configuration of transition metals** is $(n-1)d^{1-9}ns^{1-2}$.

Fe, Cu, Ag and Au are among the transition elements that have played important roles in the development of human civilisation.

The elements constituting the *f*-block are those in which 4*f* and 5*f*-orbitals are progressively filled in the latter two long periods; these elements are formal members of group 3 from which they have taken out to form a separate *f*-block of the period table. The name **inner transition** metals are often used to refer to the elements of *f*-block elements.

The inner transition elements such as Th, Pa and U are excellent sources of nuclear energy in modern times.

Table 6.1 Outer electronic configurations of the transition elements (ground state)

[Group]	III B 3	IV B 4	V B 5	VI B 6	VII B 7	VIII B 8	VIII B 9	VIII B 10	I B 11	II B 12
1st or 3d Series										
21	22	23	24	25	26	27	28	29	30	
Sc Scandium	Ti Titanium	V Vanadium	Cr Chromium	Mn Manganese	Fe Iron	Co Cobalt	Ni Nickel	Cu Copper	Zn Zinc	
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10
2nd or 4d Series										
39	40	41	42	43	44	45	46	47	48	
Y Yttrium	Zr Zirconium	Nb Niobium	Mo Molybdenum	Tc Technetium	Ru Ruthenium	Rh Rhodium	Pd Palladium	Ag Silver	Cd Cadmium	
5s	2	2	1	1	1	1	0	1	2	
4d	1	2	4	5	6	7	8	10	10	10
3rd or 5d Series										
57	72	73	74	75	76	77	78	79	80	
La Lanthanum	Hf Hafnium	Ta Tantalum	W Tungsten	Re Rhenium	Os Osmium	Ir Iridium	Pt Platinum	Au Gold	Hg Mercury	
6s	2	2	2	2	2	2	1	1	2	
5d	1	2	3	4	5	6	7	9	10	10
4th or 6d Series										
89	104	105	106	107	108	109	110	111	112	
Ac Actinium	Rf Rutherfordium	Db Dubnium	Sg Seaborgium	Bh Bohrium	Hs Hassium	Mt Meitnerium	Ds Darmstadtium	Rg Roentgenium	Cn Copernicium	
7s	2	2	2	2	2	2	2	1	2	
6d	1	2	3	4	5	6	7	8	10	10

6.2 CLASSIFICATION OF d-BLOCK ELEMENTS

These are divided into four transition series:

1. **The first transition series (3d-series)** involves the filling of 3*d*-orbitals and has 10 elements from scandium ($Z = 21$) to zinc ($Z = 30$) in the fourth period.

- The second transition series (4d-series)** involves the filling of 4d-orbitals and has 10 elements from yttrium ($Z = 39$) to cadmium ($Z = 48$) in the fifth period.
- The third transition series (5d-series)** involves the filling of 5d-orbitals and has 10 elements. The first element of this series is lanthanum ($Z = 57$). It is followed by 14 elements (lanthanides or lanthanons involving filling of 4f-orbitals). The next nine elements are from hafnium ($Z = 72$) to mercury ($Z = 80$).
- The fourth transition series (6d-series)** involves the filling of 6d-orbitals and is incomplete starting from actinium ($Z = 89$) and extend up to element with atomic number 104.

6.3 ELECTRONIC CONFIGURATION OF d-BLOCK ELEMENTS

- Electronic configuration of d-block elements:** The general electronic configuration of these elements are $(n-1)^{1-10} ns^{1-2}$. The $(n-1)$ stands for inner (i.e. penultimate) d-orbitals, have 1–10 electrons and outermost ns orbitals have 1–2 electrons.
- In the representative elements (s and p-block elements), the valence electrons are present only in the outermost shell while in the transition elements, the valence electrons are present in the outermost shell as well as in the inner d-orbitals i.e., penultimate shell.
- Due to very little difference in the energies of $(n-1)d$ and ns orbitals, the electrons from both these orbitals may be involved in bond formation.

6.3.1 EXCEPTIONAL ELECTRONIC CONFIGURATION IN 3d SERIES

In 3d transition elements, the exceptions are observed in the electronic configuration of Cr ($Z = 24$) and Cu ($Z = 29$).

- Expected electronic configuration of Cr ($Z = 24$) and Cu ($Z = 29$) are $[\text{Ar}] 3d^4 4s^2$ and $[\text{Ar}] 3d^9 4s^2$ respectively.
- The observed electronic configuration of Cr and Cu are, $[\text{Ar}] 3d^5 4s^1$ and $[\text{Ar}] 3d^{10} 4s^1$ respectively.

Explanation: The energy gap between the two sets (3d and 4s) of orbitals is small enough to prevent electron entering the 3d orbitals to attain additional stability by the atom by either having half-filled configuration (d^5) or completely filled configuration (d^{10}). The extra stability of half-filled or fully filled configuration can be explained on the basis of **exchange energy** and **symmetrical distribution of electrons**.

6.3.2 EXCEPTIONAL ELECTRONIC CONFIGURATION IN 4d AND 5d TRANSITION ELEMENTS

In 4d and 5d series, the valence electronic configuration of Mo ($Z = 42$) ($4d^5 5s^1$), Pd ($Z = 46$) ($4d^{10} 5s^0$), Ag ($Z = 47$) ($4d^{10} 5s^1$),

Pt ($Z = 78$) ($5d^9 6s^1$) and Au ($Z = 79$) ($5d^{10} 6s^1$) are explained on the basis of the concept that half-filled and completely filled d-orbitals are relatively more stable than the other d-orbitals.

On the basis of the above concept it is, however, not easy to explain the irregularities found in the observed electronic configurations of the atoms of other elements, since one has to consider the net effect of so many other factors such as (i) nuclear attraction, (ii) shielding of one electron by several other electrons, (iii) inter-electronic repulsion, (iv) the exchange-energy forces etc. All these factors play an important part together in determining the final stability of an electronic configuration of an atom.

The properties of transition elements of any given period are not so much different from one another as those of the same period of non-transition elements. The reason of this fact lies in the electronic configuration of transition elements. The electronic configuration of transition elements is invariably $(n-1)d^{1-10} ns^{1-2}$ which indicates that (i) the electronic configurations of transition elements differ from one another only in the number of electrons in d orbitals in the $(n-1)$ th shell and (ii) the number of electrons in the outermost shell, ns, is invariably 1 or 2.

6.3.3 Zn, Cd AND Hg NOT REGARDED AS TRANSITION ELEMENTS

Strictly speaking, transition elements are those elements which have incompletely filled $(n-1)$ d-orbitals in its ground state or in any one of its oxidation state.

The valence electronic configuration of Zn, Cd, Hg and their ions (e.g. Zn^{2+} , Cd^{2+} and Hg^{2+}) are as follows:

Zn ($Z = 30$):	$3d^{10} 4s^2$,	$\text{Zn}^{2+} = 3d^{10}$
Cd ($Z = 48$):	$4d^{10} 5s^2$,	$\text{Cd}^{2+} = 4d^{10}$
Hg ($Z = 80$):	$5d^{10} 6s^2$,	$\text{Hg}^{2+} = 5d^{10}$

The $(n-1)$ d-orbitals in these elements and their dipositive ions are completely filled, therefore they are not regarded as transition elements. They do not show properties of transition elements to any appreciable extent except for their stability to form complexes. However, being the end elements of three transition series, they are generally studied with the d-block elements.

6.3.4 Cu, Ag AND Au REGARDED AS TRANSITION ELEMENTS

Although the $(n-1)$ d-orbitals in these elements are completely filled, yet they are considered as transition elements. This is due to the fact that $(n-1)$ d-orbitals of these elements in their common oxidation states are incompletely filled. For example,

Element	Valence E.C.	Less stable O.S.	More stable O.S.
Cu ($Z = 29$)	$3d^{10} 4s^1$	$\text{Cu}^{\oplus}: 3d^{10}$	$\text{Cu}^{2+}: 3d^9$
Ag ($Z = 47$)	$4d^{10} 5s^1$	$\text{Ag}^{\oplus}: 4d^{10}$	$\text{Ag}^{2+}: 4d^9$
Au ($Z = 79$)	$5d^{10} 6s^1$	$\text{Au}^{\oplus}: 5d^{10}$	$\text{Au}^{3+}: 5d^8$

Obviously, Cu and Cu^{\oplus} (cupric ion), Ag and Ag^{\oplus} and Au and Au^{\oplus} ions cannot be considered as transition elements and

that is why they do not exhibit the characteristic properties of the transition elements. However Cu^{2+} (cupric ion), Ag^{2+} and Au^{3+} ion has incomplete $(n-1)d$ -orbitals, and hence these elements are regarded as transition elements.

ILLUSTRATION 6.1

On what ground can you say that scandium ($Z=21$) is a transition element but zinc ($Z=30$) is not?

Sol. On the basis of incompletely filled $3d$ orbitals in case of scandium atom in its ground state ($3d^1$), it is regarded as a transition element. On the other hand, zinc atom has completely filled d -orbitals ($3d^{10}$) in its ground state as well as in its oxidised state, hence it is not regarded as a transition element.

6.4 GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

1. The d -orbitals are more influenced by the surrounding and also affect the atom or molecule surrounding them, because d -orbitals of the transition elements project to the periphery of an atom more than s and p -orbitals. Hence, the d -electrons affect the properties of elements to a great extent. Thus ions with similar d^n configuration ($n = 1 - 9$) have similar magnetic and electronic properties.
2. There are greater horizontal similarities in the properties of the transition elements in contrast to main group elements. However, some group similarities also exist.
3. All transition elements show typical metallic properties such as malleability and ductility, high tensile strength, high thermal and electrical conductivity and metallic lustre.
4. With the exception of Zn, Cd, Hg and Mn they have one or more typical metallic (lattice) structure at normal temperatures, as shown in Table 6.2.

Table 6.2 Lattice structures of transition metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
hcp (bcc)	hcp (bcc)	bcc	bcc (bcc, ccp)	X (hcp)	bcc (hcp)	ccp	ccp	ccp	X (hcp)
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
hcp (bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X (hcp)
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
hcp (ccp, bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X

Note: (bcc = body centred cubic; hcp = hexagonal close packed; ccp = cubic close packed; X = a typical metal structure)

5. Their atomic radii are in-between those of s and p -block elements. In a series, they decrease with increase in atomic number but the decrease is small after midway.
6. They have high melting and boiling points, high enthalpies of vaporisation, high enthalpies of atomisation and high

enthalpies of hydration of their ions. These properties depend upon the strength of the metallic bond in them.

7. Their first ionisation energies are higher than those of s -block elements and less than those of p -block elements.
8. They show variable oxidation states.
9. The stability of any oxidation state or the tendency for a transition metal ion to act as oxidising or reducing agent depends upon its electrode potential.
10. They are electropositive in nature.
11. Most of the transition elements form coloured compounds.
12. Their compounds are generally paramagnetic in nature.
13. A number of these transition metals and their compounds show catalytic properties.
14. They form interstitial compounds with elements like H, C, B and N.
15. They form alloys.
16. They have a great tendency to form complexes.

6.5 METALLIC CHARACTER

All the transition elements exhibit all the characteristics of metals. For example they are hard lustrous, malleable and ductile, have high melting and boiling points, high thermal and electrical conductivity and high tensile strength.

Explanation: Transition elements have relatively low ionisation energies and have one or two electrons in their outermost energy level (ns^1 or ns^2). As a result, metallic bonds are formed. Hence, they behave as metals. The unpaired d electrons also result in the formation of metallic bonds. Thus, in the formation of metallic bonds, both ns and $(n-1)d$ electrons participate. Greater the number of unpaired d electrons, stronger is the bonding due to the overlapping of unpaired electrons between different metal atoms. Cr, Mo and W have maximum number of unpaired d electrons and are, therefore, hard metals whereas Zn, Cd and Hg are not very hard metals due to the absence of unpaired electrons.

6.6 MELTING AND BOILING POINTS

The transition metals have very high melting and boiling points. The melting points of the transition metals rise to a maximum and then fall as the atomic number increases. Manganese and technetium have abnormally low melting points (Fig. 6.1).

Explanation: Strong metallic bonds between the atoms of these elements are responsible for the high melting and boiling points. This is clear from their high enthalpies of atomisation (i.e., heat required to break the metal lattice to get free atoms).

Table 6.3 Enthalpies of atomisation of first transition series.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
326	473	575	397	281	416	425	430	339	126

The metals of the second ($4d$) and third ($5d$) series have greater enthalpies of atomisation than the corresponding elements of the first series (Fig. 6.2). This is an important factor for their having much more frequent metal-metal bonding in their compounds.

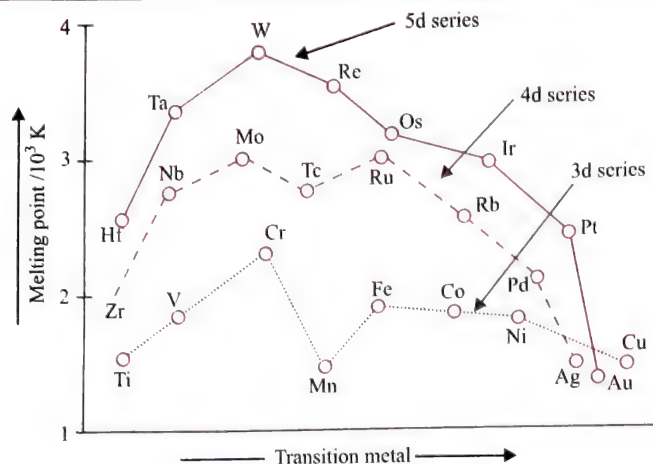


Fig. 6.1 Melting points of transition metals

Greater is the number of unpaired electrons stronger is the metallic bonding. Because of the stronger metallic bonding, these elements have high melting and boiling points.

In a particular series, the metallic strength increases up to the middle with increasing number of unpaired electrons, i.e., up to d^5 configuration. After Cr, the number of unpaired electrons goes on decreasing. Accordingly, the melting points decrease after middle (Cr) because of increasing pairing of electrons.

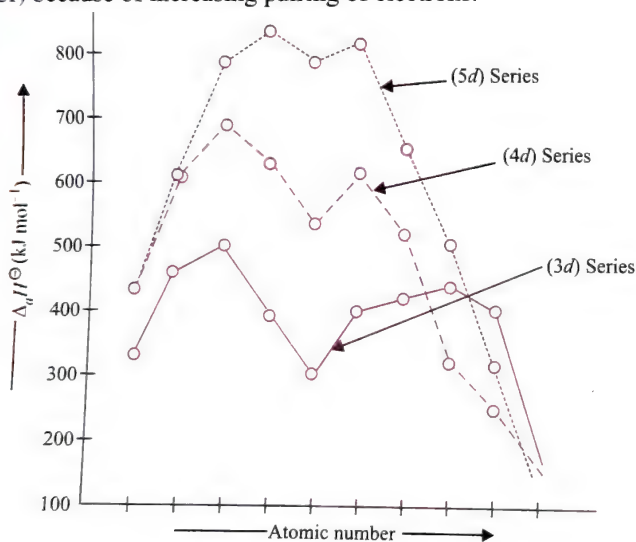


Fig. 6.2 Enthalpies of atomisation of transition metals

Note: Note that tungsten (W) has the highest melting point among the d-block elements.

The dip in the melting point at Mn in the first transition series and at Tc in the second transition series and somewhat in Re in the third transition series can be explained on the basis that they have exactly half-filled d -orbitals. As a result, in each case, the electronic configuration is stable, i.e., electrons are held tightly by the nucleus so that the delocalisation is less and the metallic bond is much weaker than that preceding element.

6.7 ATOMIC AND IONIC RADII

1. The atomic radii of the transition metals lie in-between those of s - and p -block elements.

2. Generally the atomic radii of d -block elements in a series decrease with increase in atomic number but the decrease in atomic size is small after midway. In the first transition series, the atomic radii decrease from Sc to Cr but after that it remains almost same. At the end of the transition series, there is a small increase in atomic radii (Table 6.4).

Table 6.4 Atomic radii of d -block elements in pm

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
164	147	135	129	131	126	125	125	128	137
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
180	160	146	129	136	134	134	137	144	154
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
187	158	146	139	137	135	136	138	144	157

Note: Circled elements have almost same atomic radii due to the consequence of lanthanide contraction.

Explanation: The observed irregular trend in the atomic radii of the transition metals can be explained by the following factors:

- (i) Z_{eff} (effective nuclear charge) and (ii) Shielding effect due to increasing number of d -electrons.
 - i. Z_{eff} :** In general, transition elements along a given series shows a progressive decrease in the atomic radius due to increase in Z_{eff} .
 - ii. Shielding effect of d -electrons:** This is because the extra electron enters a d -orbital each time the nuclear charge increases by unity. The shielding effect of a d -electron is small. The net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases. The atomic radii also decrease in the same way.
 - iii.** In the beginning, the atomic radius decreases with the increase of atomic number (Z) because of shielding effect of d -electrons is small and increases with increase of d -electrons.
 - iv.** The decrease within the series is quite small because in atomic radius due to increase in nuclear charge is partly cancelled by the increase in the atomic radius due to shielding effect provided by the electrons being added in the inner d -orbitals.
 - v.** As a result, the atomic radii remain practically same after chromium. For example, in Fe, the two opposing tendencies almost counterbalance and there is no change in the size from Mn to Fe. Same type of behaviour is found in second ($4d$) and third ($5d$) transition series (Table 6.4). At the end of the period, there is a slight increase in the atomic radii.
- Explanation:** Near the end of series, the increased electron-electron repulsions between added electrons in the same orbitals are greater than the attractive forces due to the increased nuclear charge. This results in the expansion of the electron cloud and thus the atomic radius increases.
- vi.** The atomic radii increase down the group. The atomic radii of second ($4d$) series are larger than those of

first (3d) transition series. But the atomic radii of the second (4d) and third (5d) transition are almost the same (Figure 6.3).

Explanation: This is due to the intervention of the 4f orbitals, which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbitals results in a regular decrease in atomic radii called **lanthanoid contraction** which compensates for the expected increase in atomic size with increasing atomic number. Thus the increase in normal size from Sc → Y → La disappears after the lanthanides. The net result of lanthanoid contraction is that the pairs of element such as Zr/Hf, Nb/Ta and Mo/W are almost identical in size. The close similarity of properties in such a pair makes chemical separation very difficult.

The sizes of the third (5d) row of transition elements are very similar to those of the second (4d) row of transition elements. Thus 4d and 5d elements resemble each other more closely than do the first (3d) and second (4d) row.

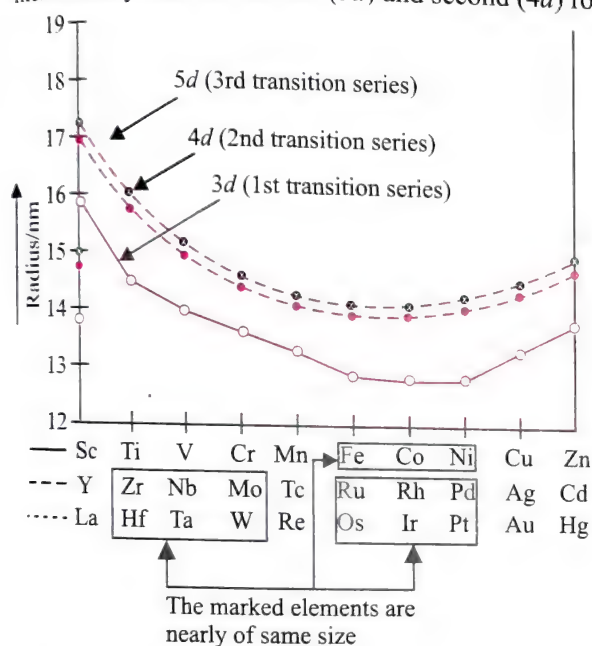


Fig. 6.3 Trends in atomic radii of transition element of lanthanide contraction

Ionic radii:

- In general, the ionic radii decrease with increase in oxidation state. Thus, the ionic size of M^{3+} cations are smaller than those of M^{2+} cations. This is because the ionic radius decreases with increase in (Z_{eff}) effective nuclear charge. However, the ionic radii of cations in the same oxidation state decrease with the increase in atomic number (see Table 6.5).
- The ionic radii of the transition metals are smaller than those of s and p block elements of the same period.

Note: s and p block elements form positive ions, whereas p-block elements form negative ion.

ILLUSTRATION 6.2

Why do the transition elements exhibit higher enthalpies of atomisation ?

Sol. Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomisation.

6.8 DENSITY

Along the transition series, the decrease in atomic radii or decrease in metallic radius/atomic radius coupled with increase in atomic mass results in general increase in density (Table 6.5).

Thus, from Ti ($Z = 22$) to Cu ($Z = 29$) there is a significant increase in the densities of these elements.

Zn is an exception having large atomic volume and hence lower density.

Among d-block elements Sc has lowest (3.43 g cm^{-3}) and Ir has highest (22.61 g cm^{-3}) densities. Os and Ir have almost same densities.

Table 6.5 Electronic configurations and some other properties of the first series of transition elements

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Atomic number	21	22	23	24	25	26	27	28	29	30	
Electronic configuration											
M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$	
M^{\oplus}	$3d^1 4s^1$	$3d^2 4s^1$	$3d^3 4s^1$	$3d^5$	$3d^5 4s^1$	$3d^6 4s^1$	$3d^7 4s^1$	$3d^8 4s^1$	$3d^{10}$	$3d^{10} 4s^1$	
M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$	
M^{3+}	$3d^0$	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	—	—	
Enthalpy of atomisation, $\Delta_a H^{\ominus}/\text{kJ mol}^{-1}$											
	326	473	515	397	281	416	425	430	339	126	
Ionisation enthlapy/ $\Delta_i H^{\ominus}/\text{kJ mol}^{-1}$											
$\Delta_i H^{\ominus}$	I	631	656	650	653	717	762	758	736	745	906
$\Delta_i H^{\ominus}$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H^{\ominus}$	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829

Metallic / ionic radii / pm

M	164	147	135	129	137	126	125	125	128	137
M ²⁺	—	—	79	82	82	77	74	70	73	75
M ³⁺	73	67	64	62	65	65	61	60	—	—

Standard Electrode Potential E°/V

M ²⁺ /M	—	-1.63	-1.18	-0.90	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76
M ³⁺ /M ²⁺	—	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	—	—	—
Density/g cm ⁻³	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

6.9 OXIDATION STATE

All the transition elements, except the first and last member of the series, show a great variety of oxidation states in its compounds, as shown in Table 6.6.

Explanation: The transition elements have a tendency to show variable oxidation states (O.S.) because of very small difference in the energies of $(n-1)d$ and ns orbitals. Therefore, both energy levels are used for chemical bond formation.

In simple compounds, +2 O.S. are obtained by the removal of 2 electrons from ns orbital and $(n-1)d$ remain unaffected. But the higher O.S. like +3, +4, +5, +6 and +7 are obtained by the removal of electrons from both $(n-1)d$ and ns orbitals.

Some observations:

- The most common O.S. of 3d series elements is +2, except for Sc = +3, +2 O.S. is obtained by the removal of ns^2 electron. This implies that $(n-1)d$ orbitals are more stable than ns^2 orbitals after Sc.
- The number of O.S. shown by the elements along the transition series first increases till middle as the number of unpaired electrons increases after that it starts decreasing as the electrons start getting paired.

- At the other end, the only O.S. of Zn is +2, since no d -electrons are involved ($3d^{10}$ configuration).
- Maximum value of O.S. for any transition element is found in its compound with F and O, as they are small in size and most EN (electronegative elements).
- Transition elements in lower O.S. (i.e. +2 and +3) form ionic compounds while in higher O.S. form covalent compounds (**Fajan's rule**). Because higher O.S. covalent bonds are formed by sharing d electrons. For example, in MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, all the bonds formed between Mn and oxygen in MnO_4^- and between Cr and oxygen in $\text{Cr}_2\text{O}_7^{2-}$ are covalent.
- The elements which show the greatest number of oxidation states occur in or near the middle of the series. For example, Mn shows all the oxidation states from +2 to +7. The lesser number of oxidation states on the extreme ends are either due to too few electrons to lose or share (e.g., Sc, Ti) or too many d -electrons so that fewer orbitals are available to share electrons with others (e.g., Cu, Zn). The highest oxidation state shown by any transition metal is +8 (by osmium).

Table 6.6 Generally shown oxidation states of transition metals (very rare oxidation states are given in parentheses and most common ones are enclosed in boxes for first transition series)

3d Series	Z	21	22	23	24	25	26	27	28	29	30
		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			(+2)	+2	+2	+2	+2	+2	+2	+1	+2
		+3	+3	+3	+3	+3	+3	+3	+3	+2	
			+4	+4	+4	+4	+4	+4	+4		
				+5	+5	+5					
					+6	+6					
						+7	(+6)				
4d Series	Z	39	40	41	42	43	44	45	46	47	48
		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
		+3	(+3)	(+2)	+2	+2	+2	+2	+2	+1	+2

Series

d- and f- Block Elements 6.1										
		+4	(+3)	+3	(+4)	+3	+3	(+3)	(+2)	
				(+4)	+4	(+5)	+4	+4	+4	(+3)
				+5	+5		(+5)	(+6)		
					+6		(+6)			
							(+7)			
							(+8)			
Z	71	72	73	74	75	76	77	78	79	80
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
					(+1)					
	+3	(+3)	(+2)	+2	(+2)	+2	+2	+2	+1	+1
		+4	(+3)	(+3)	(+3)	+3	+3	(+3)	(+3)	+2
			(+4)	+4	+4	+4	+4	+4		
			+5	+5	+5	+6	(+6)	(+5)		
				+6	(+6)	+8		(+6)		
					+7					

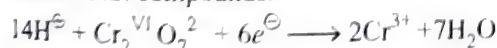
vi. The maximum oxidation states of reasonable stability in the first transition series is equal to the sum of s and d electrons up to Mn followed by an abrupt decrease in the stability of higher oxidation states.

vii. The variability of oxidation states of transition elements, which is due to incompletely filled d -orbitals, arises in such a way that successive oxidation states differ by unity, e.g., V^{II} , V^{III} , V^{IV} , V^V . This is unlike non-transition elements where oxidation states normally differ by two units, e.g., Pb^I , Pb^{IV} , Sn^{II} , Sn^{IV} etc.

viii. In a group of d -block elements, the higher oxidation states are more stable for heavier elements.

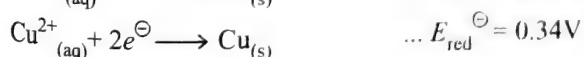
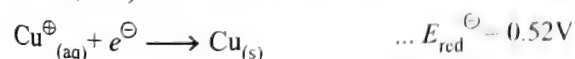
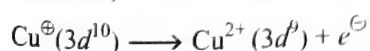
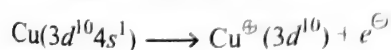
For example, in group 6, Mo (VI) and W (VI) are found to be more stable than Cr (VI). For this reason, Cr(VI) in the form of dichromate is a stronger oxidising agent in acidic medium whereas MoO_3 and WO_3 are not. Although in the p -block the lower O.S. are more stable for heavier members due to inert pair effect, e.g. in 13, 14 and 15 groups Tl, Pb and Bi are more stable in +1, +2, and +3 O.S. respectively.

For example, the following reaction undergoes reduction hence acts as strong oxidising agent. $Mo^{VI}O_3$ and $W^{VI}O_3$ are stable in +6 O.S. and thus do not undergo reduction to give lower O.S. compounds.



ix. Relative stabilities of transition elements in different O.S. is also determined from their electrode reduction potential value.

For example, Cu exists in +1 and +2 O.S. as Cu^{\oplus} and Cu^{2+} .



Thus, Cu^{2+} is more stable than Cu^{\oplus} since

$$E_{Cu^{\oplus}_{(aq)}/Cu_{(s)}}^{\ominus} > E_{Cu^{2+}_{(aq)}/Cu_{(s)}}^{\ominus}$$

Thus, Cu^{\oplus} is reduced more easily than Cu^{2+} .

xi. Low oxidation states are found when a complex compound has ligands (like CO) capable of π -acceptor character in addition to the σ -bonding. This is due to synergic bonding. For example, Cu in $CuCl$ is in +1 O.S. whereas Ni in $Ni(CO)_4$ and Fe in $Fe(O)_5$ both are in zero O.S.

xii. The oxidation state of a metal in a solvent depends on the nature of the solvent. The metal in a particular oxidation state may undergo oxidation or reduction in the solvent under appropriate conditions.

For example, Cu^{\oplus} is unstable in water it may undergo oxidation whereas Cu^{2+} is stable in water. Similarly, Fe^{2+} is unstable in aerated water (water in which air is dissolved) as it undergoes oxidation in it

ILLUSTRATION 6.3

- Phosphorous (P_4) and vanadium (V) both exhibit variable oxidation states but due to different reason. Explain.
- Name the transition metal which does not show variable O.S.

Sol.

a. In phosphorous (P_4) it is due to inert pair effect, whereas in vanadium (V) it is due to the participation of d -orbital electrons.

b. Scandium (Sc) ($Z = 21$); $3d^1 4s^2$

Sc^{2+} ; $3d^1 \Rightarrow$ Highly unstable, does not exist.

Sc^{3+} ; $3d^0 \Rightarrow$ Noble gas configuration, stable and exist.

Therefore Sc shows only +3 O.S.

6.10 IONISATION ENTHALPIES (IE) OR ($\Delta_f H^\ominus$)

- There is a gradual increase in ionisation enthalpies (IE) along a transition series from left to right, though some irregularities are observed (Table 6.5).
- The first ionisation enthalpies (IE₁) of transition elements lie between *s*- and *p*-block elements. They are higher than those of *s*-block elements and are lower than those of *p*-block elements.

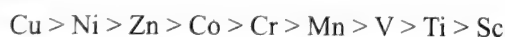
Explanation:

- Due to increase in nuclear charge with increase in atomic number (*Z*), the size of atom decreases and IE (or $\Delta_f H^\ominus$) increases.
- The irregular trend in the IE₁ (or $\Delta_f H^\ominus$) of the 3d elements is due to the fact that the removal of electron alters the relative energies of 4*s* and 3*d* orbitals. There is thus, a **reorganisation energy** accompanying ionisation. This results into the release of **exchange energy** which increases as the number of *d*-electrons increases in the *dⁿ* configuration and also from the transference of *s*-electrons into *d*-orbitals.
- IE₁ (or $\Delta_f H^\ominus$) of Cr is lower because there is no change in the *d* configuration and gives stable configuration (3*d*⁵)
Cr (*Z* = 24): $3d^5 4s^1 \longrightarrow Cr^\oplus(3d^5) + e^\ominus$
- IE₁ (or $\Delta_f H^\ominus$) of Zn is higher because the electron is lost from 4*s* level of the stable configuration.
Zn (*Z* = 30): $3d^{10} 4s^2 \longrightarrow Zn^\oplus(3d^{10} 4s^1) + e^\ominus$

Stable configuration

- IE₂ and IE₃, generally increase along the transition series, and usually are much higher, with some exceptions.

Explanation: Unusually high IE₂ values are due to attainment of stable configuration of M²⁺ ions in which the configuration of M[⊕] ions are disrupted, with considerable loss of exchange energy. Thus decreasing order of IE₂ of 3d series is



- IE₁ of 5*d* elements are higher than those of 3*d* and 4*d* elements. This is due to the imperfect (weak) shielding of one electron by another in the same set of orbitals. However, the shielding of one 4*f* electron by another is less than that of one *d*-electron by another and as the nuclear charge increases along the series, there is fairly increase in IE₁ of 5*d* elements. The IE of 3*d* and 4*d* elements are irregular.

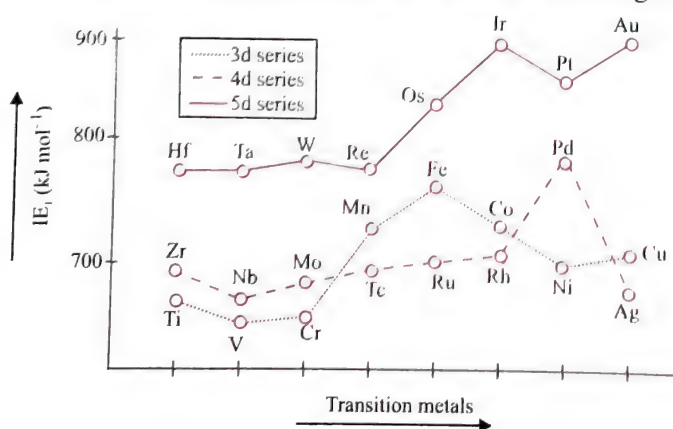


Fig. 6.4 Ionisation enthalpies of transition metals. IE₁ of 5*d* metals are higher than those of 3*d* and 4*d* metals

ILLUSTRATION 6.4

- Why IE₁ of Zn, Cd and Hg are very high?
- The relative difference in IE of any two consecutive *d*-block elements is smaller than those of *s* and *p*-block elements.
- IE₂ is unusually very high for Cr and Cu. Why?

Sol.

- It is due to completely filled and stable configuration, i.e. $(n-1)d^{10}ns^2$ configuration.
- This is because they involve gradual filling up of inner *d*-orbitals due to which increase in nuclear charge is partly cancelled by shielding effect provided by "inner" *d*-electrons.
- This is because after the removal of first electron Cr and Cu acquire a stable configuration (*d*⁵ and *d*¹⁰) and the removal of second electron is very difficult.

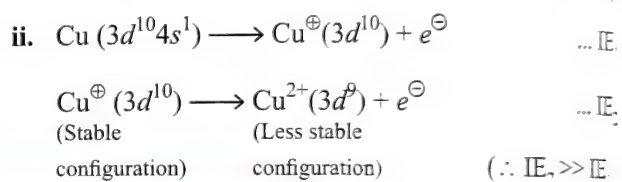
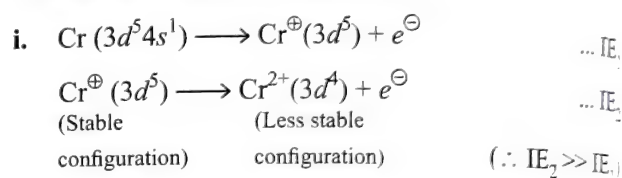
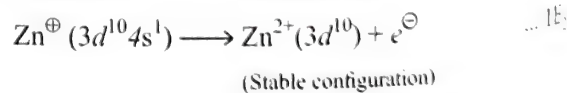
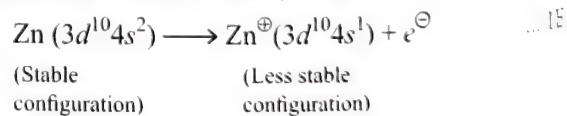


ILLUSTRATION 6.5

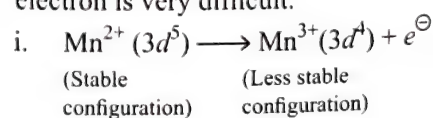
- IE₂ for Zn is comparatively lower as compared to Cu and Ni.
- IE₃ of Mn and Zn are very high. Why?
 - IE₃ for change from Fe²⁺ to Fe³⁺ is very small.
 - IE₃ of Mn is higher than that of Fe. Why?
 - Why Cu, Ni and Zn have a maximum oxidation state of +2?

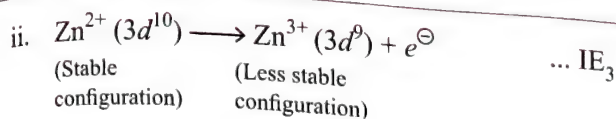
Sol.

- This is because Zn[⊕](3*d*¹⁰ 4*s*¹) will readily lose an electron to acquire stable 3*d*¹⁰ configuration.

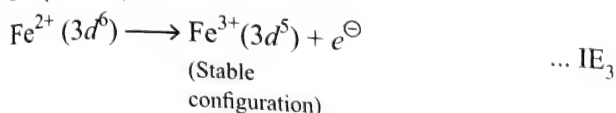
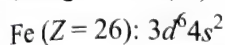


- Mn (*Z* = 25): 3*d*⁵ 4*s*² Zn (*Z* = 30): 3*d*¹⁰ 4*s*²
The trend in IE₃ is not complicated by the absence of *d* orbital in M²⁺ ions. This is because after the removal of second electron Mn and Zn acquires stable configuration of *d*⁵ and *d*¹⁰ respectively and hence removal of third electron is very difficult.



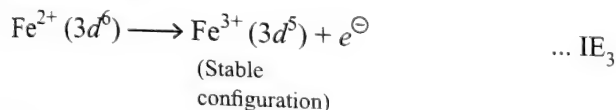
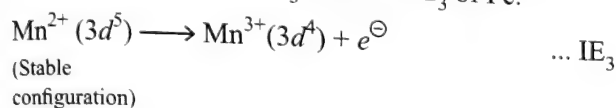


- b. This is because the loss of third electron gives the stable configuration (d^5)



- c. $\text{Mn} (Z = 25): 3d^5 4s^2$; $\text{Fe} (Z = 26): 3d^6 4s^2$
 $\text{Mn}^{2+}: 3d^5$ $\text{Fe}^{2+}: 3d^6$

After the removal of second electron, Mn^{2+} and Fe^{2+} acquire a configuration of $3d^4$ and $3d^5$ respectively. Thus to remove an electron from $3d^5$ is more difficult than from $3d^6$. Hence IE_3 of $\text{Mn} > \text{IE}_3$ of Fe .



- d. The high values of IE_3 for



explains why they have a maximum oxidation of +2.

ILLUSTRATION 6.6

- a. $\text{K}_2[\text{Ni}^{\text{II}}\text{Cl}_4]$ exists while corresponding Pt compound $\text{K}_2[\text{Pt}^{\text{II}}\text{Cl}_4]$ is unknown. Why?
 b. $\text{K}_2[\text{Pt}^{\text{IV}}\text{Cl}_6]$ exists while corresponding Ni compound $\text{K}_2[\text{Ni}^{\text{IV}}\text{Cl}_6]$ is unknown. Why?

Sol.

- a. IE explains about relative stabilities of various oxidation states.

For example, Ni^{2+} compounds are more stable than Pt^{2+} compounds, e.g.,

	$\text{IE}_1 + \text{IE}_2 \text{ (kJ mol}^{-1}\text{)}$	
Ni	2.49	Smaller the $(\text{IE}_1 + \text{IE}_2)$ of the metal more stable is its compound. \therefore Stability: $\text{Ni}^{2+} > \text{Pt}^{2+}$
Pt	2.66	

In case of Pt high $(\text{IE}_1 + \text{IE}_2)$ value is due to imperfect shielding effect of 4f-orbitals. This shielding effect increases the attraction between nucleus and outermost electron and hence $(\text{IE}_1 + \text{IE}_2)$ of Pt is more.

- b. $(\text{IE}_1 + \text{IE}_2 + \text{IE}_3 + \text{IE}_4)$ is lower for Pt.

High $(\text{IE}_3 + \text{IE}_4)$ value for Ni is due to very small size of Ni^{3+} and Ni^{4+} in comparison to Pt^{3+} and Pt^{4+} .

Hence stability of $\text{Pt}^{4+} > \text{Ni}^{4+}$.

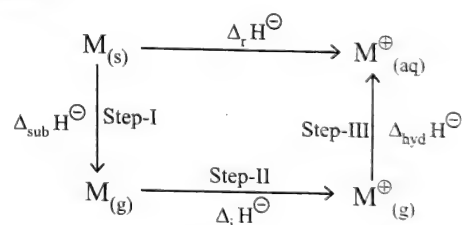
	$\text{IE}_3 + \text{IE}_4 \text{ (kJ mol}^{-1}\text{)}$	$\text{IE}_1 + \text{IE}_2 + \text{IE}_3 + \text{IE}_4 \text{ (kJ mol}^{-1}\text{)}$
Ni	8.80	$2.49 + 8.8 = 11.29$
Pt	6.70	$2.66 + 6.70 = 9.36$

6.11 STANDARD ELECTRODE POTENTIAL (E^\ominus_{red})

- Thermodynamic stability of the compounds of transition elements is determined by the magnitude of IE of transition elements. If IE of the element is lower, more stable is its compounds.
- In solution, the stability of the compounds depends on electrode potential, which depends upon the following factors:
 - Enthalpy of sublimation of the element ($\Delta_{\text{sub}} H^\ominus$).
 - Ionisation enthalpy of the element (IE or $\Delta_i H^\ominus$).
 - Hydration enthalpy of the element ($\Delta_{\text{hyd}} H^\ominus$).
- The total enthalpy of the process ($\text{M}_{(\text{s})} \longrightarrow \text{M}^\oplus_{(\text{aq})} + e^\ominus$) is the sum of three types of enthalpies i.e.,

$$\Delta_r H^\ominus = \Delta_{\text{sub}} H^\ominus + \Delta_i H^\ominus + \Delta_{\text{hyd}} H^\ominus$$

The above steps are represented by Born Haber cycle as follows.



Thus electrode potential is a measure of $\Delta_r H^\ominus$. Hence quantitatively, the stability of transition metal ions in different O.S. is determined by the electrode potential.

The above process represents $E^\ominus_{\text{M(s)/M}^\oplus(\text{aq})}$, i.e., oxidation potential and the reverse process i.e., $E^\ominus_{\text{M}^\oplus(\text{aq})/\text{M(s)}}$, represents the reduction potential. If E^\ominus_{oxid} is more positive, the metal will undergo oxidation more easily and formation of $\text{M}^\oplus_{(\text{aq})}$ from $\text{M}_{(\text{s})}$ is more stable.

Similarly, if E^\ominus_{red} is more positive, the metal ion will undergo reduction more easily and formation of $\text{M}^\oplus_{(\text{aq})}$ from $\text{M}_{(\text{s})}$ is less stable.

Alternatively, the lower the E^\ominus_{red} value i.e. more negative E^\ominus_{red} , i.e. value of the electrode more stable is the oxidation state of the metal in the aqueous solution,

$E^\ominus_{\text{M}^{2+}/\text{M}}$ and $E^\ominus_{\text{M}^{3+}/\text{M}^{2+}}$ for 3d block elements are given in Table.

The observed and calculated values for $E^\ominus_{\text{M}^{2+}/\text{M}}$ are compared in following Figure 6.5.

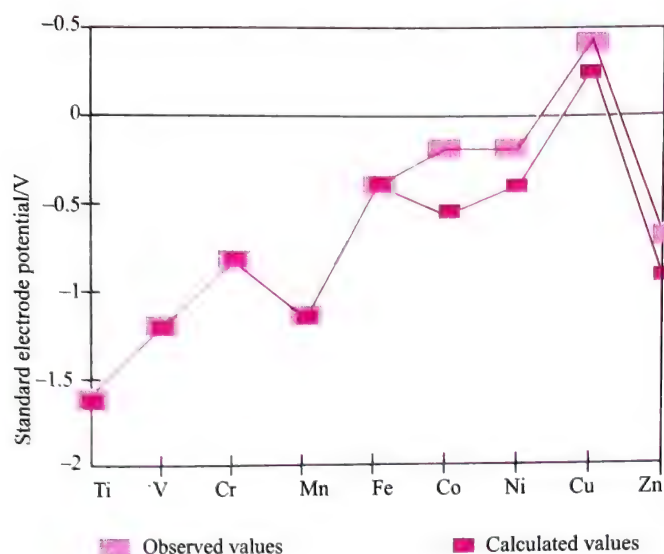


Fig. 6.5 Observed and calculated values for the standard electrode potentials ($M^{2+} \rightarrow M^0$) of elements Ti to Zn

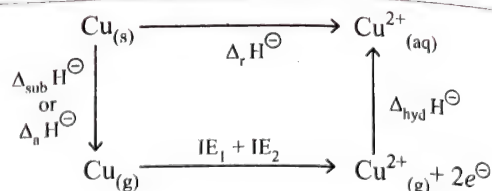
Table 6.7 Thermochemical data (kJ mol^{-1}) for the 3d series of transition elements and the standard electrode potentials for the reduction of M^{II} to M

Element (M)	$\Delta_f H^\ominus(M)$	$\Delta_f H_1^\ominus$	$\Delta_f H_2^\ominus$	$\Delta_{\text{hyd}} H^\ominus(M^{2+})$	E^\ominus/V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	+0.34
Zn	130	908	1730	-2059	-0.76

6.11.1 TRENDS IN THE $E^\ominus_{(M^{2+}/M)}$ VALUES IN 3d SERIES

- There is no regular trend in the $E^\ominus_{(M^{2+}/M)}$ values of 3d series (Table 6.5), because sum of $(IE_1 + IE_2)$ and $\Delta_{\text{sub}} H^\ominus$ do not show any regular trend.
- The general trend towards less negative $E^\ominus_{(M^{2+}/M)}$ values along the 3d series (except for $E^\ominus_{(Cu^{2+}/Cu)}$ values) is due to general increase in the sum of $(IE_1 + IE_2)$ values.
- Copper (Cu) is the only metal in 3d series which have positive $E^\ominus_{Cu^{2+}(aq)/Cu(s)}$ value, because high sum of $(IE_1 + IE_2 + \Delta_{\text{sub}} H^\ominus)$ values is not counterbalanced by low $\Delta_{\text{hyd}} H^\ominus$ value.

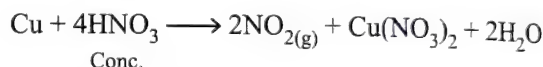
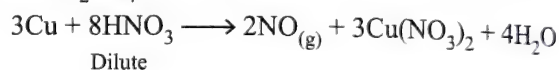
The positive $E^\ominus_{Cu^{2+}(aq)/Cu(s)}$ value suggests that reduction of $Cu^{2+}_{(aq)}$ to $Cu_{(s)}$ is favourable. For example,



If the oxidation reaction from $Cu_{(s)}$ to $Cu^{2+}_{(aq)}$ is favourable, then it should have low sum of $(IE_1 + IE_2 + \Delta_{\text{sub}} H^\ominus)$ values and more negative $\Delta_{\text{hyd}} H^\ominus$ value.

But the reverse process i.e. reduction of $Cu^{2+}_{(aq)}$ to $Cu_{(s)}$ is favourable because of high sum of $(IE_1 + IE_2 + \Delta_{\text{sub}} H^\ominus)$ values and less negative $\Delta_{\text{hyd}} H^\ominus$ value.

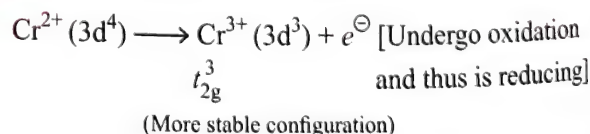
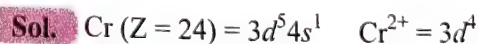
- $E^\ominus_{M^{2+}(aq)/Mn(s)}$ values of all the transition elements (except Cu in 3d series) is lower (negative) than that of hydrogen (taken as zero). Thus all the transition elements, with negative reduction potential liberate $H_{2(g)}$ from dilute acids. But Cu does not liberate $H_{2(g)}$ from dilute acids. Cu is inert towards non-oxidising acids, but reacts with conc. HNO_3 and H_2SO_4 .



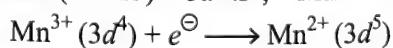
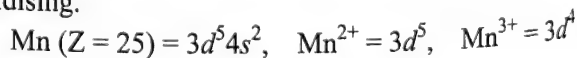
- The value of $E^\ominus_{M^{2+}(aq)/M(s)}$ for Mn, Ni and Zn are more negative than expected from the general trend (Table 6.5). This is due to greater stability of half-filled d-subshell (d^5) in Mn^{2+} and completely filled d-subshell (d^{10}) in Zn^{2+} , e.g.
 - $Mn (Z=25) (3d^5 4s^2) \rightarrow Mn^{2+} (3d^5) \dots E^\ominus_{\text{red}} = -1.18V$ (Stable)
 - $Zn (Z=30) (3d^{10} 4s^2) \rightarrow Zn^{2+} (3d^{10}) \dots E^\ominus = -0.76V$ (Stable)
- The exceptional $E^\ominus_{Ni^{2+}(aq)/Ni(s)}$ value from the regular trend is due to its high negative $\Delta_{\text{hyd}} H^\ominus$ value.

ILLUSTRATION 6.7

Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration?



Cr^{2+} undergoes oxidation and hence is reducing as its configuration changes from d^4 to d^3 , the latter having a half filled t_{2g} level. On the other hand, the reduction of Mn^{3+} to Mn^{2+} results in the half-filled ($3d^5$) configuration which has extra stability, and thus is oxidising.



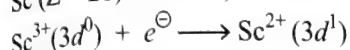
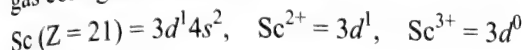
(More stable configuration)

[Undergo reduction and thus is oxidising]

6.11.2 TRENDS IN THE $E^\ominus (M^{3+}/M^{2+})$ VALUES OF 3d SERIES

$E^\ominus (M^{3+}/M^{2+})$ values of 3d-elements show the varying trends. (Table 6.5). More high positive ($E^\ominus_{M^{3+}/M^{2+}}$) value shows that reduction of M^{3+} to M^{2+} occurs very easily. This accounts for stronger oxidising properties of M^{3+} ion.

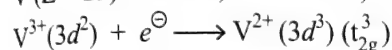
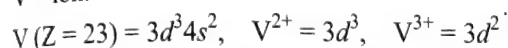
1. The very low value for $E^\ominus_{(Sc^{3+}/Sc^{2+})}$ is due to stable noble gas configuration of Sc^{3+} ion.



(Stable configuration)

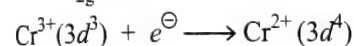
2. The comparatively low negative value for

$E^\ominus_{V^{3+}/V^{2+}} = -0.26V$, is due to half stable t_{2g}^3 configuration of V^{2+} ion.



(Stable configuration)

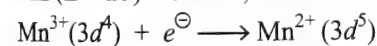
3. The comparatively high negative $E^\ominus_{Cr^{3+}/Cr^{2+}} = -0.41V$, is due to more stable configuration of Cr^{3+} ion having a half-filled t_{2g}^3 level.



(More stable t_{2g}^3 configuration)

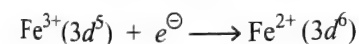
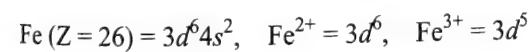
(Less stable configuration)

4. The comparatively high positive value for $E^\ominus_{(Mn^{3+}/Mn^{2+})} = +1.57V$, is due to very stable (d^5) configuration of Mn^{2+} ion.



(Stable configuration)

5. The comparatively low positive value for $E^\ominus_{(Fe^{3+}/Fe^{2+})} = +0.77V$, is due to stable configuration of Fe^{3+} ($3d^5$) ion.

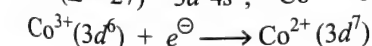
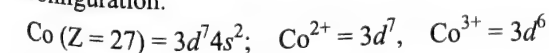


(Stable configuration)

Although from electronic configuration, reduction of Fe^{3+} (d^5) to Fe^{2+} (d^6) is not very favourable yet low positive E^\ominus_{red} value favours the reduction of Fe^{3+} to Fe^{2+} ion to some extent.

Due to high charge density of Fe^{3+} ion, high (negative) hydration enthalpy ($\Delta_{hyd}H^\ominus$) favours the reduction of Fe^{3+} to Fe^{2+} ion.

6. Exceptional high positive $E^\ominus_{(Co^{3+}/Co^{2+})} (+1.97V)$ value cannot be explained satisfactorily by electronic configuration.

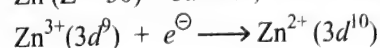
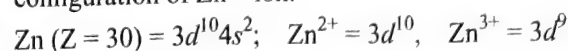


The stabilities of d^6 and d^7 configuration cannot be compared. The extra stability of Co^{2+} (d^7) configuration

and high positive $E^\ominus_{Co^{3+}/Co^{2+}}$ value is related to the highest negative enthalpy of hydration ($\Delta_{hyd}H^\ominus$). In 3d series, size of Co^{3+} ion is 61 pm, therefore charge density is very high. Hence have highest negative $\Delta_{hyd}H^\ominus$ value.

7. Similarly, high positive $E^\ominus_{Ni^{3+}/Ni^{2+}}$ value can be related to the high negative enthalpy of hydration ($\Delta_{hyd}H^\ominus$).

8. The highest positive value (not given in Table 6.5) of $E^\ominus_{(Zn^{3+}/Zn^{2+})}$ is due to very high stable full filled ($3d^{10}$) configuration of Zn^{2+} ion.



(Very stable configuration)

It is difficult to remove an electron from Zn^{2+} ion to change it into +3 state.

6.12 CHEMICAL REACTIVITY AND E^\ominus VALUES

The transition metals vary widely in their chemical reactivity. Some of them are highly electropositive and dissolve in mineral acids whereas a few of them are 'noble', i.e., they do not react with simple acids.

Some results of chemical reactivity of transition metals as related to their E^\ominus values are given below:

1. The metals of the 3d-series (except copper) are relatively more reactive than the other series. Thus, they are oxidised by H^\oplus ions though the actual rate is slow, e.g., Ti and V are passive to dilute non-oxidising acids at room temperature.
2. Less negative E^\ominus values for Mn^{2+}/Mn along the series indicate a decreasing tendency to form divalent cations.
3. More, negative E^\ominus values than expected for Mn, Ni and Zn show greater stability for Mn^{2+} , Ni^{2+} and Zn^{2+} .
4. E^\ominus values for the redox couple M^{3+}/M^{2+} indicate that Mn^{3+} and Co^{3+} ions are the strongest oxidising agents in aqueous solution whereas Ti^{2+} , V^{2+} and Cr^{2+} are strongest reducing agents and can liberate hydrogen from a dilute acid, e.g.,

$$2Cr^{2+}_{(aq)} + 2H^\oplus_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + H_{2(g)}$$

ILLUSTRATION 6.8

For the first row transition metals the E^\ominus values are:

E^\ominus	V	Cr	Mn	Fe	Co	Ni	Cu
(M^{2+}/M)	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Explain the irregularity in the above values.

Sol. The $E^\ominus (M^{2+}/M)$ values are not regular which can be explained from the regular variation of ionisation enthalpies ($\Delta_i H_1 + \Delta_i H_2$) and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

ILLUSTRATION 6.9

Why is the value for the Mn^{3+}/Mn^{2+} couple much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+} ? Explain.

Sol. Refer to Section 6.11.2, points (3), (4) and (5).

Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

$$E_{\text{Mn}^{3+}/\text{Mn}^{2+}}^{\ominus} > E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\ominus} > E_{\text{Cr}^{3+}/\text{Cr}^{2+}}^{\ominus} \\ (+1.57 > +0.77 > -0.41\text{V})$$

6.13 TRENDS IN STABILITY OF HIGHER OXIDATION STATES OF TRANSITION METAL HALIDES

The stable halides of the 3d series of transition metals are shown in table given below.

Table 6.8 Formulas of halides of 3d metals

Oxidation number									
+6			CrF ₆						
+5		VF ₅	CrF ₆						
+4	TiX ₄	VX ₄ ^I	CrX ₄	MnF ₄					
+3	TiX ₃	VX ₃	CrX ₃	MnF ₃	FeX ₃ ^I	CoF ₃			
+2	TiX ₂ ^{III}	VX ₂	CrX ₂	MnX ₂	FeX ₂	CoX ₂	NiX ₂ ^{II}	CuX ₂ ^{II}	ZnX ₂
+1								CuX ^{III}	

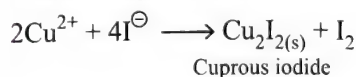
Key: X = F → I; X^I = F → Br, X^{II} = F, Cl; X^{III} = Cl → I

- i The highest oxidation states vary from +4 for Ti (in TiX₄, tetrahalides) to +5 for V (VF₅) to +6 for Cr (in CrF₆), then to +7 for Mn (not in simple halides but in MnO₃F). Beyond Mn, no metal shows an oxidation state of more than +3, which is only in the trihalides, FeX₃ and CoF₃.

The highest oxidation is generally most stable with fluorine. This is due to either higher lattice energy, e.g., in CoF₃ or

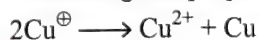
higher bond enthalpies for the higher covalent compounds, e.g., in VF₅ and CrF₆.

- ii. V directly shows an oxidation state of +5 only in VF₅, other halides, however, undergo hydrolysis to give oxohalides, VOX₃ in which oxidation state of V is +5.
- iii. In the low oxidation states, fluorides are unstable, e.g., in TiX₂, VX₂, CuX (X = Cl[⊖], Br[⊖], I[⊖]), but not F[⊖]. However, copper(II) halides are known including CuF₂ but except iodide. They oxidise iodide to iodine



That is why Cu₂I₂ exists but CuI₂ does not.

- iv. Many copper(I) compounds are unstable in aqueous solution and undergo disproportionation as follows:



The greater stability of Cu²⁺_(aq) than Cu[⊕]_(aq) is due to much more negative enthalpy of hydration for Cu²⁺_(aq) than Cu[⊕]_(aq). This more than compensates for the high IE₂ of Cu.

6.13.1 OXIDES OF 3d ELEMENTS AND THEIR STABILITY

Oxygen stabilises the highest oxidation state in its oxide.

- i. The highest oxidation number in the oxides is same as that of group number and is attained in Sc₂O₃ to Mn₂O₇ i.e. up to group 7.
- ii. Beyond group 7, the maximum oxidation is +3 (in Fe₂O₃), although in the ferrates, (FeO₄)²⁻, formed in the alkaline medium, Fe has oxidation state of +6. But these readily decompose to Fe₂O₃ and O₂.
- iii. Besides the oxides, higher oxidation states are also found in the oxocations, e.g., V⁵⁺ in VO₂[⊕], V⁶⁺ in VO²⁺ and Ti⁴⁺ in TiO²⁺.

Table 6.9 Oxides of 3d metals

Oxidation number	Groups									
	3	4	5	6	7	8	9	10	11	12
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+7					Mn ₂ O ₇					
+6				CrO ₃						
+5			V ₂ O ₅							
+4		TiO ₂	V ₂ O ₄	CrO ₂	MnO ₂					
+3	Sc ₂ O ₃	Ti ₂ O ₃	V ₂ O ₃	Cr ₂ O ₃	Mn ₂ O ₃	Fe ₂ O ₃				
					Mn ₃ O ₄	Fe ₃ O ₄ [*]	Co ₃ O ₄ [*]			
+2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+1									Cu ₂ O	

*Mixed oxides.

6.13.2 MnF₄ AND Mn₂O₇ EXISTS BUT MnF₇ DOES NOT

The highest Mn fluoride is MnF₄, whereas the highest oxide is Mn₂O₇. In other words in Mn fluoride the highest oxidation state of Mn is +4 but in oxides it is +7, although F is more EN than oxygen.

Thus, the ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. This is due to the ability of oxygen to form $p\pi-d\pi$ multiple bonds to metals. Vacant $3d$ -orbitals of Mn overlap with $2p$ -orbitals of oxygen to form $(p\pi-d\pi)$ multiple bonds as shown in Figure.

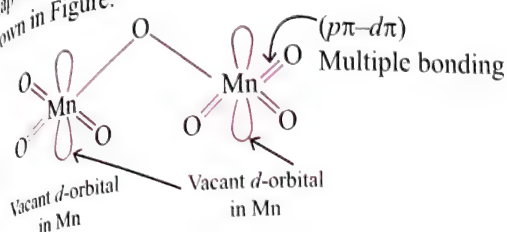


Fig. 6.6 Structure of Mn_2O_7

ILLUSTRATION 6.10

How would you account for the increasing oxidising power in the series $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$?

This is due to the increasing stability of the lower species which they are reduced.

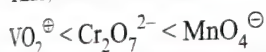
i. MnO_4^- is reduced to more stable configuration $\text{Mn}^{2+}(3d^5)$ and $\text{Mn}^{4+}(3d^3 \text{ or } t_{2g}^3)$.

Hence, it acts as strongest oxidising agent amongst the given ions.

ii. $\text{Cr}_2\text{O}_7^{2-}$ is reduced to a stable configuration $\text{Cr}^{3+}(3d^3 \text{ or } t_{2g}^3)$. Hence it acts as a stronger oxidising agent.

iii. In $(\text{VO}_2)^+$, V is in +5 O.S. having $3d^0$ stable configuration and is therefore not reduced effectively.

Thus, the increasing oxidising power is as follows:



6.14 MAGNETIC PROPERTIES

Each element has some kind of magnetic properties associated with it. These properties have direct consequence of the electronic configuration of the atom. When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed:

(i) Diamagnetism and (ii) Paramagnetism.

1. Diamagnetic substances are weakly repelled by the magnetic applied field and have all the electrons paired in their atoms, e.g. NaCl and H_2O .

2. Paramagnetic substances are attracted by the magnetic applied field and has one or more unpaired electrons in their atoms, e.g. Cu^{2+} , Fe^{3+} , Cr^{3+} and O_2 .

Substances which are strongly attracted by the magnetic applied field are said to be **ferromagnetic**. In fact, ferromagnetism is an extreme form of paramagnetism.

3. Ferromagnetic substances keep their magnetism even after the field is removed while paramagnetic and diamagnetic substances fail to do so. Fe, Co and Ni are some examples of ferromagnetic substances.

4. Paramagnetism is due to the presence of unpaired electrons. An electron in an atom which has two types of motion, one of

its motion is about the nucleus (orbital angular momentum), and the other is its spin about its own axis (spin angular momentum).

A single electron, spinning about its own axis generates a magnetic field. For two electrons in an orbital, the spins are opposite and hence the fields cancel each other, hence they have zero magnetic moment value.

5. When there are one or more unpaired electrons in them, the unpaired electron gives rise to a magnetic field on account of its spin and because of the angular orbital moment.

6. Magnetic moment (μ_{s+L}) of the first row of transition metal ions is given by general formula:

$$\mu_{s+L} = \sqrt{4S(S+1) + L(L+1)}$$

where S is the sum of spin quantum numbers and L = sum of the orbital angular momentum quantum numbers.

For an electron, spin quantum number, $S = \pm 1/2$. Hence, $S = s \times n$ (n = number of unpaired electrons).

For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these the magnetic moment is determined by the number of unpaired electrons and is calculated by using 'spin only' formula. Taking $L = 0$, the magnetic moment is given as

$$\mu_s = \sqrt{4S(S+1)}$$

In terms of n (number of unpaired electrons), it is given by

$$\mu_s = \sqrt{n(n+2)} \text{ BM (Bohr magneton)}$$

7. It is measured in BM.

$$1 \text{ BM} = \frac{eh}{4\pi m} = 9.27 \times 10^{-21} \text{ ergs gauss}^{-1}$$

$$\text{or } 9.27 \times 10^{-24} \times \text{J Tesla}^{-1} \text{ or } 9.27 \times 10^{-24} \text{ A m}^2$$

where h is the Planck's constant, e is the electronic charge, and m is the mass of electrons.

Note: The orbital motion in $4f$ orbitals is not quenched, as in the case of d -block elements. Hence the observed paramagnetism in $4f$ -block elements is due to both orbital motion of the electron and its spinning round its axis.

$$\text{When } n = 1, \mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

$$n = 2, \mu_s = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ BM}$$

$$n = 3, \mu_s = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$$

and so on.

$\therefore \mu_s \propto n$ (number of unpaired electrons).

The magnetic moments calculated from the 'spin-only' formula and those derived experimentally for some of the ions of the first row transition elements are given in Table. The experimental data are mainly for hydrated ions in solution or in the solid state.

Table 6.10 Magnetic moments of some ions of 3d-series

Ions	Configuration	Unpaired electron(s)	Magnetic moment (BM)	
			Calculated	Observed
Sc ³⁺ (Z = 21)	Sc = 3d ¹ 4s ² ⇒ Sc ³⁺ = 3d ⁰ 4s ⁰	0	$\mu_s = \sqrt{n(n+2)} = 0$	0
Ti ³⁺ (Z = 22)	Ti = 3d ² 4s ² ⇒ Ti ³⁺ = 3d ¹ 4s ⁰	1	$\sqrt{1(1+2)} = \sqrt{3} = 1.73$	1.75
Ti ²⁺ (Z = 22)	Ti = 3d ² 4s ² ⇒ Ti ²⁺ = 3d ² 4s ⁰	2	$\sqrt{2(2+2)} = \sqrt{8} = 2.84$	2.76
V ²⁺ (Z = 23)	V = 3d ³ 4s ² ⇒ V ²⁺ = 3d ³ 4s ⁰	3	$\sqrt{3(3+2)} = \sqrt{15} = 3.87$	3.86
Cr ²⁺ (Z = 24)	Cr = 3d ⁵ 4s ¹ ⇒ Cr ²⁺ = 3d ⁴ 4s ⁰	4	$\sqrt{4(4+2)} = \sqrt{24} = 4.90$	4.80
Mn ²⁺ (Z = 25)	Mn = 3d ⁵ 4s ² ⇒ Mn ²⁺ = 3d ⁵ 4s ⁰	5	$\sqrt{5(5+2)} = \sqrt{35} = 5.92$	5.96
Fe ²⁺ (Z = 26)	Fe = 3d ⁶ 4s ² ⇒ Fe ²⁺ = 3d ⁶ 4s ⁰	4	$\sqrt{4(4+2)} = \sqrt{24} = 4.90$	5.3–5.5
Co ²⁺ (Z = 27)	Co = 3d ⁷ 4s ² ⇒ Co ²⁺ = 3d ⁷ 4s ⁰	3	$\sqrt{3(3+2)} = \sqrt{15} = 3.87$	4.4–5.2
Ni ²⁺ (Z = 28)	Ni = 3d ⁸ 4s ⁰ ⇒ Ni ²⁺ = 3d ⁸ 4s ⁰	2	$\sqrt{2(2+2)} = \sqrt{8} = 2.84$	2.9–3.4
Cu ²⁺ (Z = 29)	Cu = 3d ¹⁰ 4s ¹ ⇒ Cu ²⁺ = 3d ⁹	1	$\sqrt{1(1+2)} = \sqrt{3} = 1.73$	1.8–2.2
Zn ²⁺ (Z = 30)	Zn = 3d ¹⁰ 4s ² ⇒ Zn ²⁺ = 3d ¹⁰ 4s ⁰	0	$\sqrt{0(0+2)} = 0$	0

ILLUSTRATION 6.11

Which element in 3d, 4d and 5d transition series has the highest paramagnetism in:

- a. elemental form b. +1 O.S.
c. +2 O.S. d. +3 O.S.
[O.S. = Oxidation State]

Sol.

Group	3	4	5	6	7	8	9	10	11	12
3d	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
4d	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
5d	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg

a. In elemental form:

3d series: Cr (Z = 24) ⇒ 3d⁵4s¹; n = 6,

$$\mu = \sqrt{6(6+2)} = \sqrt{48} \text{ BM}$$

4d series: Mo (Z = 42) ⇒ 4d⁵5s¹; n = 6, $\mu = \sqrt{48} \text{ BM}$

5d series: W (Z = 74) ⇒ 5d⁴5s²; n = 4, $\mu = \sqrt{24} \text{ BM}$

But Re has the highest number of unpaired electron, as shown:

Re (Z = 75) ⇒ 5d⁵6s²; n = 5, $\mu = \sqrt{35} \text{ BM}$

b. In +1 oxidation state:

3d series: Mn (Z = 25) ⇒ 3d⁵4s²; Mn¹⁺ = 3d⁵4s¹

n = 6, $\mu = \sqrt{48} \text{ BM}$

4d series: Tc (Z = 43) ⇒ 4d⁵5s²; Tc¹⁺ = 4d⁵5s¹

n = 6, $\mu = \sqrt{48} \text{ BM}$

5d series: Re (Z = 75) ⇒ 5d⁵6s²; Re¹⁺ = 5d⁵6s¹

n = 6, $\mu = \sqrt{48} \text{ BM}$

c. In +2 oxidation state:

3d series: Mn (Z = 25) ⇒ 3d⁵4s²; Mn²⁺ = 3d⁵4s⁰

n = 5, $\mu = \sqrt{35} \text{ BM}$

4d series: Tc (Z = 43) ⇒ 4d⁵5s²; Tc²⁺ = 4d⁵5s⁰

n = 5, $\mu = \sqrt{35} \text{ BM}$

5d series: Re (Z = 75) ⇒ 5d⁵6s²; Re²⁺ = 5d⁵6s⁰

n = 5, $\mu = \sqrt{35} \text{ BM}$

d. In +3 oxidation state:

3d series: Fe (Z = 26) ⇒ 3d⁶4s²; Fe³⁺ = 3d⁵4s⁰

4d series: Ru ($Z = 44$) $\Rightarrow 4d^7 5s^1$ (exception electronic configuration)

$$\mu = \sqrt{4 \times 6 \times 5 \times 0} = 0; n = 5, \mu = \sqrt{35} \text{ BM}$$

5d series: Os ($Z = 76$) $\Rightarrow 5d^6 7s^2$; Os $^{3+} = 5d^5 7s^0$;

$$\mu = \sqrt{5 \times 4 \times 3 \times 0} = 0$$

- From the above calculations it is clear that in the elemental form (zero O.S.), group 6 has the highest μ , except W, in 5d series, but it is Re of group 7.
- In +1 O.S., group 7 has the highest μ .
 - In +2 O.S., again group 7 has the highest μ .
 - In +3 O.S., group 8 has the highest μ .

ILLUSTRATION 6.12

Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

Sol: With atomic number 25, the divalent ion in aqueous solution will have d^5 configuration (five unpaired electrons). The magnetic moment μ is

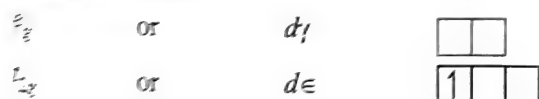
$$\mu = \sqrt{5(5+2)} = 5.92 \text{ BM}$$

6.15 FORMATION OF COLOURED IONS

Most of the transition metal compounds ionic and covalent are coloured both in solid and aqueous solution in visible light. When an electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand. In aqueous solutions where water molecules are the ligands, the colour of the ions observed are listed in table.

Note: Formation of coloured compound is due to excitation of electrons from $d \in$ to d_f or t_{2g} to e_g orbital).

In case of complex ions, d -orbitals are split into two different sets due to crystal field effect, one consisting of lower energy orbitals ($d \in$) and the other consisting of higher energy orbitals (d_f). In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, Ti has d^1 configuration and this electron is present in $d \in$ orbital in ground state.



Ground state

In absorption of yellow wavelength, the electron is excited to d_f orbital.



Absorption of yellow wavelength \rightarrow



Since yellow wavelength is absorbed from visible region of light, the blue and red light will be transmitted and solution of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ will appear purple which is the mixed effect of blue and red colours.

Sc^{3+} and Ti^{4+} have completely empty d -orbitals and are colourless. Cu^0 and Zn^{2+} have completely filled d -orbitals and there are no vacant d -orbitals for promotion of electrons, hence they are also colourless.

Table 6.11 The colours of some of the first row transition metal ions (aquated)

Configuration	Example	Colour
$3d^0$	Sc^{3+}	colourless
$3d^0$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$	Mn^{3+}	violet
$3d^4$	Cr^{2+}	blue
$3d^5$	Mn^{2+}	pink
$3d^5$	Fe^{3+}	yellow
$3d^6$	Fe^{2+}	green
$3d^7$	Co^{2+}	pink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

6.16 FORMATION OF COMPLEX COMPOUNDS

Complex compounds are formed by transition elements in contrast to such complexes are not formed by s - and p -block elements.

The transition elements form complexes due to the following reason:

1. Comparatively smaller sizes of the metal ions
2. Their high charges
3. They have high charge density (i.e., charge/size ratio)
4. Availability of vacant d -orbitals for bond formation

6.17 CATALYTIC PROPERTIES

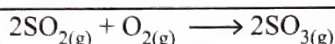
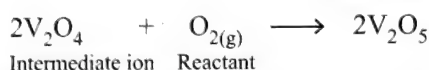
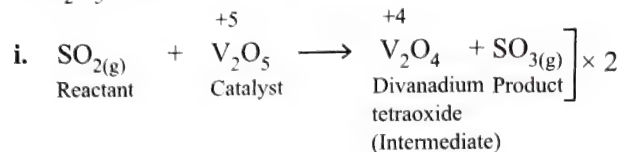
The transition metals and their compounds are used as catalysts. There are various theories to explain their catalytic activity. Some of them are summarised as:

1. **Variable oxidation theory:** The catalytic activity may be due to their variable oxidation states (incomplete d -orbitals) and hence possess the capacity to absorb and re-emit wide range of energies. This makes the required **energy of activation** available.
2. **Intermediate compound formation theory:** According to this theory, the catalyst first forms an intermediate compound with one of the reactants, which then decomposes

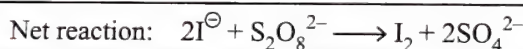
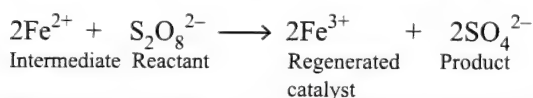
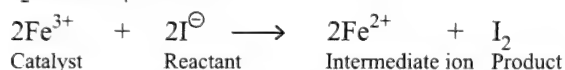
or combines with another reactants to produce the product and the catalyst is regenerated. The catalyst in this process lowers free energy of activation and hence accelerates the rate of reaction.

Note: The catalyst only provides alternative path with lower energy of activation (E_{act}). It does not change the equilibrium of the reaction.

For example, the oxidation of SO_2 to SO_3 in the presence of V_2O_5 as catalyst takes place as follows:



ii. Fe^{3+} catalyses the reaction between iodide (I^-) and persulphate or (peroxodisulphate) ($\text{S}_2\text{O}_8^{2-}$) ions to give I_2 and SO_4^{2-} ions.



Therefore from the above examples, it can be seen that how the change in oxidation state of transition metal accelerates the rate of the reaction through the formation of intermediate compound.

In example (i) vanadium (V) changes its O.S. from +5 to +4 and again to +5.

In example (ii), iron (Fe) changes its O.S. from +3 to +2 and to +3.

Thus it can be concluded that transition metal/ions become more effective as catalysts because they can change their oxidation states.

3. Adsorption theory: Due to high density of transition metal, they have large surface area in their finely divided state. The surface of the catalyst unlike the inner part of the bulk has free valencies which provide the seat for chemical forces of attraction.

Thus, catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first series of transition metals utilise 3d and 4s electrons for bonding). As a result, the concentration of the reactants on the surface of catalyst increases. Moreover, bonds in the reacting molecules become weaker and thereby the energy of activation (E_{act}) is lowered. Hence the rate of reaction increases.

6.17.1 CATALYSTS IN INDUSTRY

Some of the important catalytic processes are listed in table to give an idea about the utility of catalysts in industries.

Table 6.12 The utility of catalysts in industries

Process	Catalyst
1. Haber's process for the manufacture of ammonia $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$	Finely divided iron, molybdenum as promotor; condition: 200 bar pressure and 723–773 K temperature. Nowadays, a mixture of iron oxide, potassium oxide, and alumina is used.
2. Ostwald's process for the manufacture of nitric acid $4\text{NH}_{3(g)} + 5\text{O}_{2(g)} \rightarrow 4\text{NO}_{(g)} + 6\text{H}_2\text{O}_{(g)}$ $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{2(g)}$ $4\text{NO}_{2(g)} + 2\text{H}_2\text{O}_{(l)} + \text{O}_{2(g)} \rightarrow 4\text{HNO}_{3(aq)}$	Platinised asbestos; temperature 573 K.
3. Contact process for the manufacture of sulphuric acid $2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{SO}_{3(g)}$ $\text{SO}_{3(g)} + \text{H}_2\text{SO}_{4(aq)} \rightarrow \text{H}_2\text{S}_2\text{O}_7(aq)$ Oleum $\text{H}_2\text{S}_2\text{O}_7(l) + \text{H}_2\text{O}_{(l)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{SO}_{4(aq)}$	Platinised asbestos or vanadium pentoxide (V_2O_5); temperature 673–723 K.

6.18 FORMATION OF NON-STOICHIOMETRIC COMPOUNDS AND INTERSTITIAL COMPOUNDS

Formation of interstitial compounds:

1. Interstitial compounds are those which are formed when small atoms like H, N, C or B are trapped inside the crystal lattices of metals. They are usually non-stoichiometric and are neither typically ionic nor covalent.

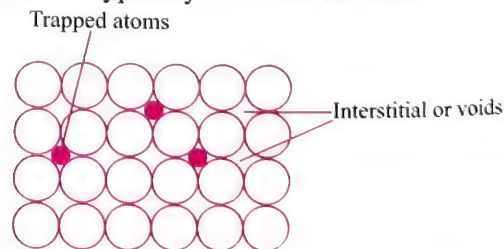


Fig. 6.7 Formation of interstitial compounds

2. These small atoms enter into the void sites between the packed atoms of the crystalline metal, e.g., TiC , Mn_4N , Fe_3H , TiH_2 , etc. The formulae quoted do not, of course, correspond to any normal oxidation state of the metal and often non-stoichiometric material is obtained with such composition as $\text{VH}_{0.56}$ and $\text{TiH}_{1.7}$, $\text{Fe}_{0.98}\text{O}$, $\text{Fe}_{0.86}\text{S}$.
3. Because of the nature of their composition, these compounds are referred to as interstitial compounds. The principal

physical and chemical characteristics of these compounds are as follows:

- They have high melting points, higher than those of pure metals.
- They are very hard, some borides approach diamond in hardness.
- They retain metallic conductivity.
- They are chemically inert.

6.19 ALLOY FORMATION

- An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15% of each other.

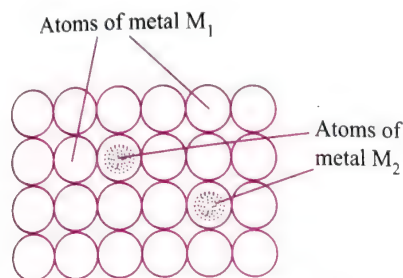


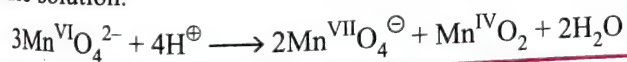
Fig. 6.8 Formation of alloys

- Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. But the melting point of alloys is less than their individual metals.
- The best known examples are ferrous alloys; chromium, vanadium, tungsten, molybdenum and manganese are used for the production of variety of steels and stainless steel.

ILLUSTRATION 6.13

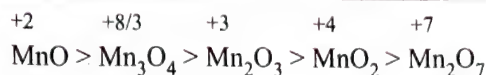
What is meant by 'disproportionation' of an oxidation state? Give an example.

Sol. When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese(VI) becomes unstable relative to manganese(VII) and manganese(IV) in acidic solution.



6.20 OXIDES AND OXOANIONS OF TRANSITION METALS

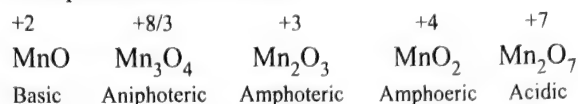
- The oxides of 3d series are generally formed from the reaction of metals with O_2 at high temperature. The oxides are formed in the oxidation states +1 to +7.
- All the metals except scandium (Sc) form the oxide with the formula MO which are ionic in nature. As the oxidation number of the metal increases, ionic character decreases, e.g., Mn_2O_7 is a covalent green oil. Even CrO_3 and V_2O_5 have low melting points.



Ionic character decreases

- In general, the oxides in the lower oxidation states of the metals are basic and in their higher oxidation states, they are acidic whereas in the intermediate oxidation state, the oxides are amphoteric.

For example, the behaviour of the oxides of manganese may be represented as follows:



Acidic character increases

Thus, Mn_2O_7 dissolves in water to give the acid HMnO_4 .

In case of vanadium, there is a gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5 though it is mainly acidic. Thus, V_2O_4 dissolves in acids to give VO^{2+} salts whereas V_2O_5 reacts with alkalis as well as acids to give VO_4^{3-} and VO_4^+ respectively.

Similarly, CrO is basic, Cr_2O_3 is amphoteric while CrO_3 is acidic, having +2, +3 and +6 OS respectively.

Thus, CrO_3 dissolves in water to give the acids H_2CrO_4 and $\text{H}_2\text{Cr}_2\text{O}_7$.

- Oxides are insoluble in water. However, basic and amphoteric oxides dissolve in non-oxidising acids like HCl to form hydrated ions $[\text{M}(\text{H}_2\text{O})_6]^{n+}$. Some of the oxides dissolve in acids and bases to form oxometallic salts, such as CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- .

- They are highly coloured (generally black).
- Polymeric in structure rather than purely ionic.

5. Oxides of first two transition metals:

- Basic oxides:** Sc_2O_3 , TiO , Ti_2O_3 , VO , V_2O_3 , MnO , FeO , Fe_2O_3 , Fe_3O_4 , CoO , NiO , Cu_2O
- Acidic oxides:** V_2O_5 , CrO_3 , Mn_2O_7
- Amphoteric oxides:** TiO_2 , VO_3 , Cr_2O_3 , CrO_2 , Mn_2O_3 , Mn_3O_4 , MnO_2 , CuO

Note: Some other types of oxides like mixed oxides, non-stoichiometric oxides and spinels are also formed by transition metals. CoMoO_4 and ZnFe_2O_4 are simple mixed oxides. Some mixed oxides contain same metal ion in two different oxidation states, e.g., Fe_3O_4 contains two oxides (FeO and Fe_2O_3) in which Fe has +2 and +3 oxidation states respectively. Mn_2O_3 is also a mixed oxides of MnO and MnO_2 .

The oxides of iron such as $\text{Fe}_{0.91}\text{O}$ and $\text{Fe}_{0.95}\text{O}$ are non-stoichiometric oxides as in these oxides iron metal ratio is not in whole number.

Spinel is special types of oxides in which oxygen atoms have face centred cubic (fcc) lattice. For example,

ZnFe_2O_4 is a normal spinel in which the trivalent (Fe^{3+}) ions occupy the octahedral sites while divalent (Zn^{2+}) ions occupy the tetrahedral sites. The spinel $\text{Fe}(\text{Fe}_2)\text{O}_4$ is an inverse spinel as in it the trivalent (Fe^{3+}) ions occupy the tetrahedral sites.

6.21 COMPARISON OF THE FIRST TWO TRANSITION METALS THROUGH THE d-ELECTRON CONFIGURATION

	d^0	d^1	d^2	d^3
i.	Sc^{3+} , Ti^{4+} , V^{5+} , Cr^{6+} and Mn^{7+}	Except V^{4+} others with d^1 configuration are either reducing or disproportionate.	Ti^{2+} to Fe^{6+} , V^{3+} and $\text{Ti}^{2+} \Rightarrow$ is reducing	Only Cr^{3+} is stable and forms complexes
ii.	But Fe^{8+} is unknown	e.g. Cr^{5+} and Mn^{6+} $3\text{CrO}_4^{3-} + 8\text{H}^+ \rightarrow 2\text{CrO}_4^{2-} + \text{Cr}^{3+} + 4\text{H}_2\text{O}$ $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$	$\text{Fe}^{6+} \Rightarrow$ is strongly oxidising $\text{V}^{3+} \Rightarrow$ is also reducing	
	d^4	d^5	d^6	d^7
	Really no stable species Strongly reducing $\text{Cr}^{2+} \Rightarrow$ Strongly reducing $\text{Mn}^{3+} \Rightarrow$ Disproportionates	Mn^{2+} and Fe^{3+} Fe^{3+} is reduced to Fe^{2+}	Fe^{2+} and Co^{3+} $\text{Fe}^{2+} \Rightarrow$ Stable and mild reducing agent $\text{Co}^{3+} \Rightarrow$ Stable in presence of strong complexing reagents	$\text{Co}^{2+} \Rightarrow$ Stable in aq. soln. $\text{Co}^{2+} \rightarrow \text{Co}^{3+} + e^-$ is oxidised in presence of strong ligands
	d^8	d^9	d^{10}	
	Ni^{2+} is the most important	This configuration is found in Cu^{2+} compounds	Cu^+ and Zn^{2+} are important Zi^{2+} is the only state known for zinc Cu^+ is readily oxidised to Cu^{2+}	

6.21.1 GENERAL GROUP TRENDS IN THE CHEMISTRY OF d-BLOCK METALS

Group: 3	Group: 4	Group: 5
Scandium (Sc) (21) Yttrium (Y) (39) Lanthanum (La) (57)	Titanium (Ti) (22) Zirconium (Zr) (40) Hafnium (Hf) (72)	Vanadium (V) (23) Niobium (Nb) (41) Tantalum (Ta) (73)
They are studied along with lanthanoids	i. They are lustrous, silvery white metals with high m. pt.	i. Shining silvery metals
	ii. Electropositive but less than group 3	ii. Less electropositive than groups 4 and 3
	iii. On heating reacts with most non-metals (O_2 and H_2) and Ti reacts with N_2	iii. Size of Nb \approx Ta (Due to consequence of lanthanoid contraction). Shows similar properties
	iv. No effect of cold acid (except HF)	iv. Shows all O.S. from +1 to +5
	v. Stable O.S. is +4	v. V^{4+} is most stable
	vi. Lower O.S. for Zr and Hf not known	vi. Nb^{5+} and Ta^{5+} are most stable.
	vii. Compounds are: TiCl_4 , ZrCl_4 , HfCl_4 , TiO_2 , ZrO_2 , HfO_2	vii. V shows all O.S. from +5 to +2
	viii. Zr and Hf (160 and 159 pm) of almost same size show similar properties	viii. V is used to increase the strength and toughness of steel
Group: 6	Group: 7	Group: 8
Chromium (Cr) (24) Molybdenum (Mo) (42) Tungsten (W) (74)	Manganese (Mn) (25) Technetium (Tc) (43) Rhenium (Re) (75)	Iron (Fe) (26) Ruthenium (Ru) (44) Osmium (Os) (76)
i. Silvery, lustrous, soft (when pure)	i. They are obtained from fission waste	i. Ru and Os are stable to atmospheric attack
ii. Shows +6 O.S. in oxo anions	ii. Re is rare, resembles Tc in properties	ii. Ru and Os show +8 O.S.
iii. Cr^{3+} as most stable and reducing	iii. Mn shows +2 to +7 O.S.	iii. Fe does not show +8 O.S.

iv. In Mo and W, strong M-M bonding	iv. Important O.S. of Mn are +2 and +4.	iv. Fe show +2 and +3 O.S.
v. Cr is used in lather industry and for making, stainless steel and chrome plating	v. Mn is used in all steels	v. Fe is used in steel
vi. Mo is used in X-ray tubes Compounds of Mo and W are used as catalysts	vi. Re is used in electronic filaments, high temp. thermocouples and flash bulbs	
Group: 9	Group: 10	Group: 11
Cobalt (Co) (27) Rhodium (Rh) (45) Iridium (Ir) (77)	Nickel (Ni) (28) Palladium (Pd) (46) Platinum (Pt) (78)	Copper (Cu) (29) Silver (Ag) (47) Gold (Au) (79)
i. Co shows +2 and +3 O.S.	i. Unreactive at normal temperature	i. Reactivity decreases down the group
ii. But +3 O.S. in aq. soln. is a strong oxidising agent	ii. Ni and Pd reacts with halogens on heating	ii. Au is inert and resembles Pt. in reactivity
iii. It can oxidise even H ₂ O with evolution of H ₂	iii. Reactivity decreases from Ni to Pd and to Pt	iii. Cu shows +2, Ag shows +1 and Au shows +3 O.S. in aq. soln.
iv. Rh and Ir show +3 O.S.	iv. Ni and Pd show +2 O.S.	iv. 1E ₁ for Ag is lowest
v. Ir shows occasionally +4 O.S.	v. Pt shows +2 and +4 O.S.	v. 1E ₁ + 1E ₂ + 1E ₃ is lowest for Au
vi. Co ³⁺ form complexes with N-donor ligands	vi. Ni is used as alloy Nichrome (60% Ni + 40% Cr) German silver (Cu 25–30%), (Zn 25–30%) (Ni 40–50%)	vi. They are not related in their chemical behaviour
vii. Co-compounds are used in ceramics, paint and as catalyst	vii. Pt and Pd are used as catalyst	
Group: 12		
Zinc (Zn) (30), Cadmium (Cd) (48) Mercury (Hg) (80)		
i. Zn and Cd are similar in their reactivity Hg shows different reactivity		
ii. All have d ¹⁰ configuration		
iii. Hg ²⁺ exists as Hg ₂ ²⁺		
iv. Because of filled d ¹⁰ configuration They show few properties of transition elements		

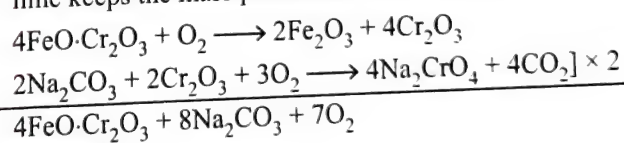
6.22 SOME IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS CONTAINING OXOANIONS

6.22.1 POTASSIUM DICHROMATE (K₂Cr₂O₇)

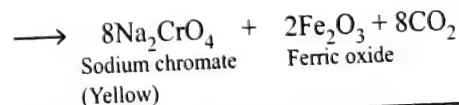
Preparation: It is prepared from the ore called chromite or ferrochrome or chrome iron, FeO·Cr₂O₃ or FeCr₂O₄ by the following steps.

- Preparation of sodium chromate:** The ore is finely powdered, mixed with sodium carbonate and quick lime and then roasted, i.e., heated to redness in a reverberatory furnace with free exposure to air when sodium chromate (yellow in

colour) is formed and carbonate dioxide is evolved. Quick lime keeps the mass porous and thus facilitates oxidation.

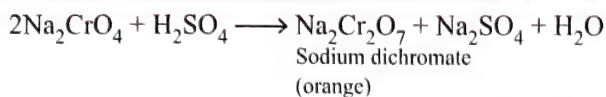


Chromite ore



The fused mass is extracted with water and filtered.

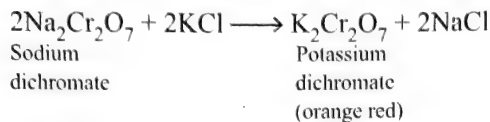
- Conversion of sodium chromate into sodium dichromate:** The filtrate containing sodium chromate solution is treated with conc. H₂SO₄ when Na₂CrO₄ is converted into Na₂Cr₂O₇·2H₂O



Na_2SO_4 being less soluble crystallises out as decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and is removed.

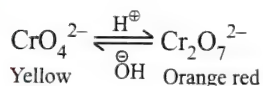
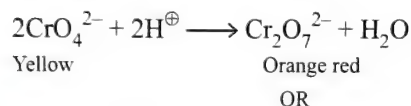
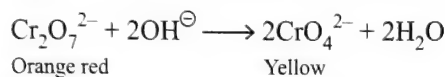
3. Conversion of $\text{Na}_2\text{Cr}_2\text{O}_7$ into $\text{K}_2\text{Cr}_2\text{O}_7$ (orange red):

$\text{Na}_2\text{Cr}_2\text{O}_7$ is more soluble than $\text{K}_2\text{Cr}_2\text{O}_7$. The latter is then prepared by treating the solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ with KCl.



Properties:

- $\text{K}_2\text{Cr}_2\text{O}_7$ is orange red crystal, melting point 669 K, moderately soluble in cold water but freely soluble in hot water.
- The chromates and dichromates are interconvertible in aqueous solution and $\text{Cr}_2\text{O}_7^{2-}$ ions are invariably in equilibrium with CrO_4^{2-} ions at pH = 4, i.e.

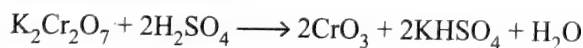


On adding an alkali (i.e., increasing the pH of solution), the H^+ ions are used up and according to the law of chemical equilibrium, the reaction proceeds in the forward direction producing yellow chromate solution. On the other hand, when an acid is added (i.e., pH of the solution is decreased), the concentration of H^+ ions is increased and the reaction proceeds in the backward direction producing an orange red dichromate solution.

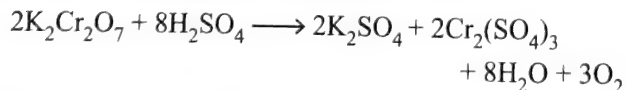
The oxidation state of chromium in chromate and dichromate is same, i.e., +6.

3. Action of concentrated sulphuric acid:

- In cold, red crystals of chromic anhydride (chromium trioxide) are formed.

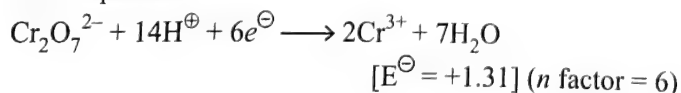


- On heating the mixture, oxygen is evolved.

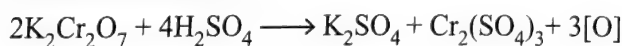


- Oxidising properties:** Potassium dichromate is a powerful oxidising agent. In acidic solution, its oxidising action can be represented as follows:

Ionic equation:



Molecular equation:

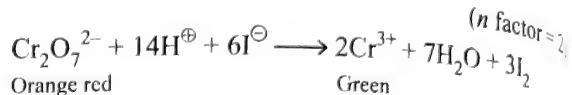


Thus, Ew of $\text{K}_2\text{Cr}_2\text{O}_7$

$$\frac{\text{Mw of } \text{K}_2\text{Cr}_2\text{O}_7}{6} = \frac{294}{6} = 49$$

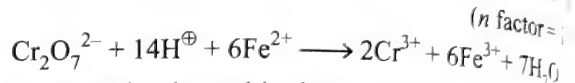
The full ionic equation is obtained by adding the half reaction for $\text{Cr}_2\text{O}_7^{2-}$ ion in acidic medium to the half reaction for the reducing agent, balancing wherever necessary.

- It oxidises iodides to iodine ($2\text{I}^- \longrightarrow \text{I}_2 + 2e^-$)



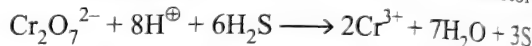
This reaction is used in the estimation of iodide ions in volumetric analysis.

- It oxidises ferrous salts to ferric salts: ($\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$)

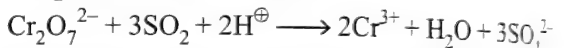
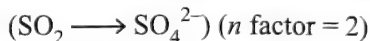


This reaction is used in the estimation of ferrous ions in the volumetric analysis.

- It oxidises H_2S to S: ($\text{S}^{2-} \longrightarrow \text{S}$)

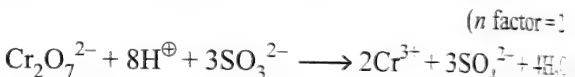


- It oxidises sulphur dioxide to sulphate ion:

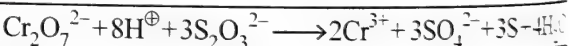
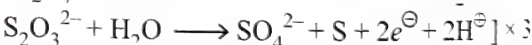
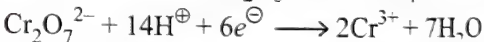
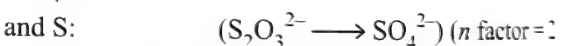


The reaction is used in the preparation of chrome alum.

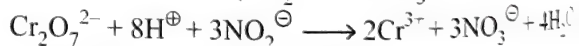
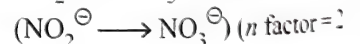
- It oxidises sulphites (SO_3^{2-}) to sulphate (SO_4^{2-}):



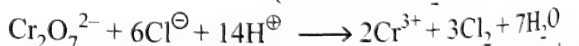
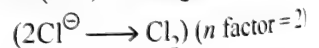
- It disproportionate thiosulphate ($\text{S}_2\text{O}_3^{2-}$) to sulphate (SO_4^{2-})



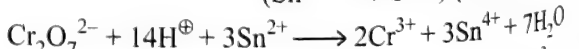
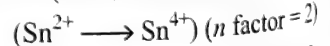
- It oxidises nitrites (NO_2^-) to NO_3^- (nitrates)



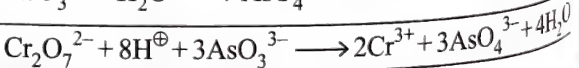
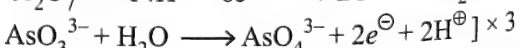
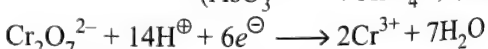
- It oxidises halogen acids (HX) to halogens



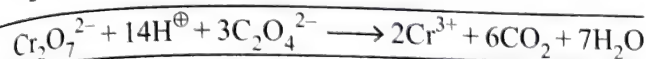
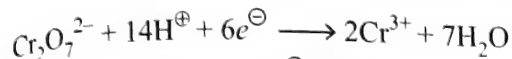
- It oxidises stannous salts (Sn^{2+}) to stannic salts (Sn^{4+})



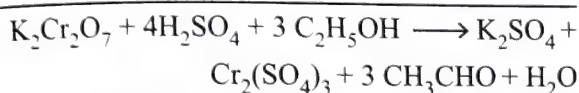
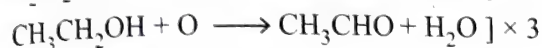
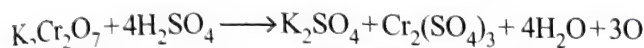
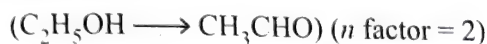
- It oxidises arsenites (AsO_3^{3-}) to arsenates (AsO_4^{3-})



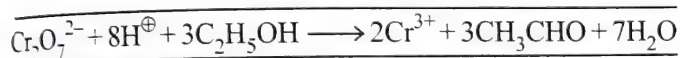
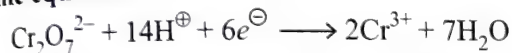
k. It oxidises oxalates ($\text{C}_2\text{O}_4^{2-}$) or oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) to CO_2 .



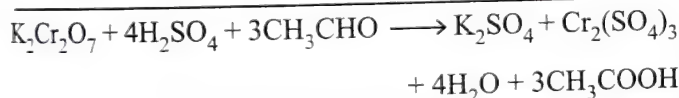
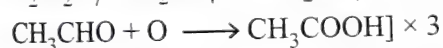
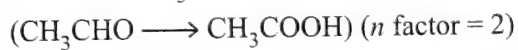
l. It oxidises ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) to acetaldehyde (or ethanal) (CH_3CHO).



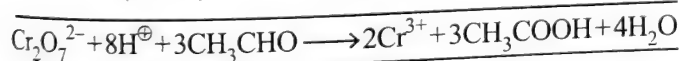
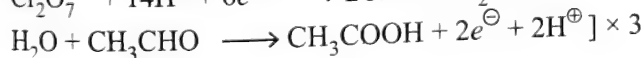
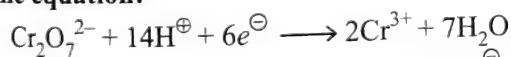
Ionic equation:



m. It oxidises acetaldehyde or ethanal (CH_3CHO) to acetic acid or ethanoic acid (CH_3COOH).

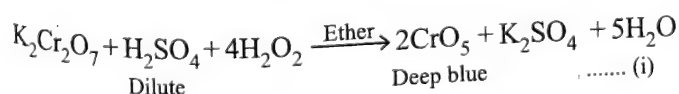
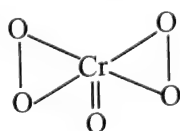


Ionic equation:

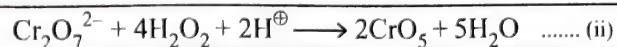
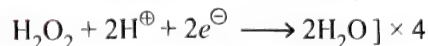
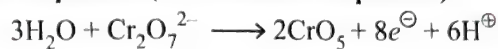


n. Reaction with H_2O_2 :

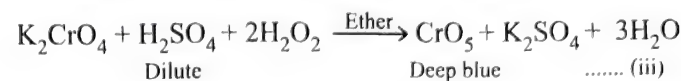
i. In this case H_2O_2 oxidises ice-cold acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution containing ether to CrO_5 (chromium diperoxide or chromic peroxide or blue perchromic acid). The ethereal layer turns intense blue in colour due to formation of CrO_5 or $[\text{CrO} \cdot (\text{O}_2)_2]$. The blue colour fades away gradually due to the decomposition of CrO_5 into Cr^{3+} ions and O_2 . The structure of CrO_5 is called butterfly structure and is shown as



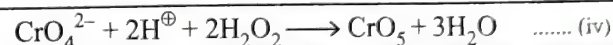
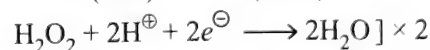
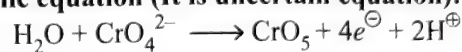
Ionic equation (It is uncertain equation):



ii. Similar reaction of H_2O_2 under similar conditions is also shown by K_2CrO_4 (potassium chromate).



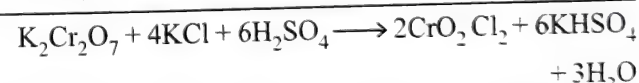
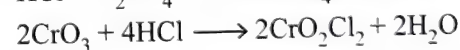
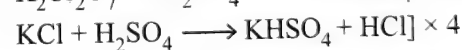
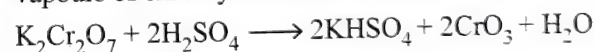
Ionic equation (It is uncertain equation):



Note:

- The molecular equations of H_2O_2 with $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} are shown in above in Eqs. (i) and (iii) respectively. In CrO_5 , O.S. of Cr = +6. But considering O.S. of Cr = +10 (which is not possible), their ionic equations are shown above in Eqs. (ii) and (iv) respectively.
- Surprisingly the result of molecular and ionic equations (i), (ii), (iii) and (iv) are same. Therefore, ionic equations (ii) and (iv) are valid.

Chromyl chloride test (Reaction with a chloride and conc. sulphuric acid). When heated with conc. HCl or with a chloride and strong H_2SO_4 , reddish brown vapours of chromyl chloride are obtained.



This reaction is used in the detection of Cl^- ions in qualitative analysis.

Note: Chlorides of Ag, Hg, Pb and Sn do not give this test.

Uses:

- In volumetric analysis, it is used as a primary standard for the estimation of Fe^{2+} (ferrous ions) and I^- (iodides) in redox titrations.

Note: $\text{Na}_2\text{Cr}_2\text{O}_7$ is not used in volumetric analysis because it is deliquescent.

- It is used in the industry.

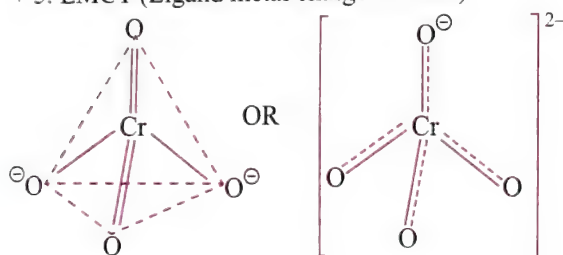
a. In the preparation of chrome alum

$\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ and other industrially important compounds such as Cr_2O_3 , CrO_3 , CrO_2O_2 , K_2CrO_4 , CrCl_3 etc.

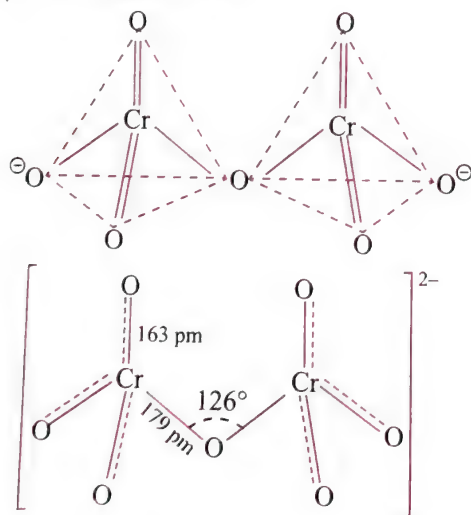
- b.** In calico printing and dyeing.
 - c.** In chrome tanning in leather industry.
 - d.** In photography and in hardening gelatine film.
- 3.** Both sodium and potassium dichromates are strong oxidizing agents. The sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry.

6.22.2 STRUCTURES OF CrO_4^{2-} AND $\text{Cr}_2\text{O}_7^{2-}$ IONS

1. In $\text{Cr}_2\text{O}_4^{2-}$ ion, Cr is sp^3 hybridised and all the Cr–O bonds are equivalent. In $\text{Cr}_2\text{O}_7^{2-}$ ion, the two Cr–O bonds which share an oxygen atom at the common vertex of two tetrahedral units are longer than the other six equivalent Cr–O bonds.
2. In CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions, Cr(VI) has d^0 configuration. Hence, yellow colour of CrO_4^{2-} and orange colour of $\text{Cr}_2\text{O}_7^{2-}$ are not due to $d-d$ transition but due to charge transfer, i.e., momentary transfer of charge from O-atom to metal atom thereby changing O^{2-} ion momentarily to O^\ominus ion and reducing the oxidation state of Cr from + 6 to + 5. LMCT (Ligand metal charge transfer)



a. CrO_4^{2-} ion-Tetrahedral structure



b. $\text{Cr}_2\text{O}_7^{2-}$ ion-Two tetrahedra sharing one oxygen atom at one corner

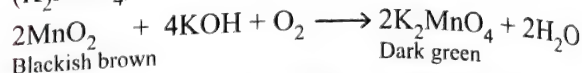
Fig. 6.9 (a) Structure of CrO_4^{2-} ion (b) Structure of $\text{Cr}_2\text{O}_7^{2-}$ ion

6.23 POTASSIUM PERMANGANATE (KMnO_4)

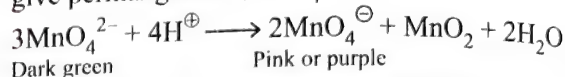
Preparation:

1. KMnO_4 is prepared by fusion of the mineral, **pyrolusite**, MnO_2 (blackish brown) with an alkali metal hydroxide (e.g. KOH) in presence of air or oxidising agent such as KNO_3 or

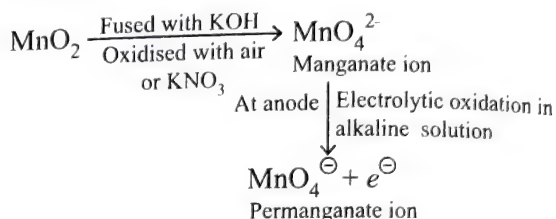
KClO_3 . This produces the dark green potassium manganate (K_2MnO_4).



2. K_2MnO_4 disproportionates in a neutral or acidic solution to give permanganate (MnO_4^-).

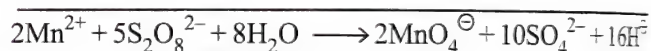
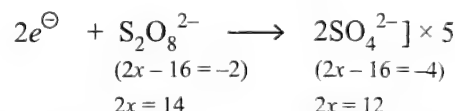
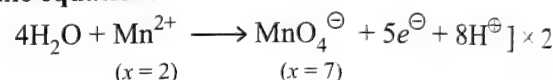


3. Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (MnO_4^{2-}) ion.



4. In the laboratory Mn^{2+} (manganese) ion salt is oxidised by peroxodisulphate ($\text{S}_2\text{O}_8^{2-}$) ion to MnO_4^- (permanganate ion).

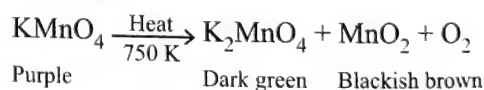
Ionic equation:



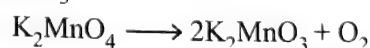
Properties:

- 1. It exists as deep purple black prisms with greenish lustre.** It is moderately soluble in water at room temperature. Its solubility increases with temperature. Its melting point is 523 K. It shows weak temperature- dependent paramagnetism. This can be explained by MOT (molecular orbital theory).

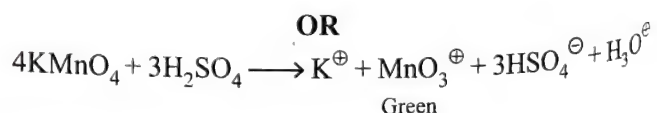
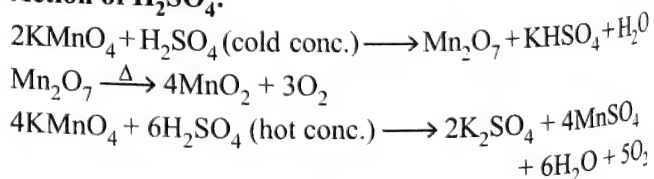
- 2. Action of heat:** It undergoes decomposition, when heated at 750 K.



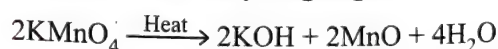
K_2MnO_4 further decomposes to give potassium manganite, K_2MnO_3 .



- ### 3. Action of H_2SO_4 :

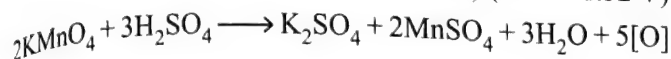
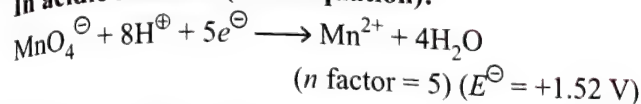


- #### 4. Action of heat in hydrogen gas:



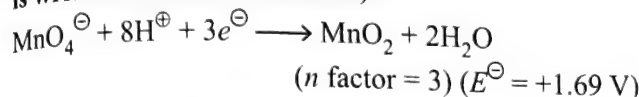
5. Oxidising properties:

a. In acidic medium (ionic equation):

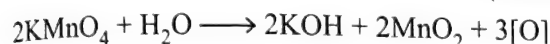
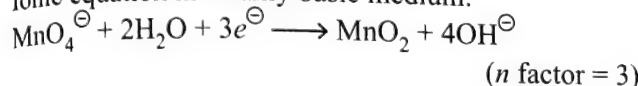


$$[E^\ominus \text{ of } \text{KMnO}_4 \text{ in acidic medium} = \frac{M_w}{5} = \frac{158}{5} = 31.6]$$

b. In weakly basic or neutral medium, (ionic equation is written in neutral medium).



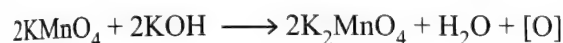
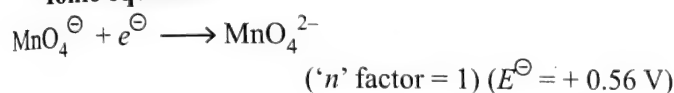
Ionic equation in weakly basic medium:



$$[E^\ominus \text{ of } \text{KMnO}_4 \text{ in neutral medium or weakly basic medium} = \frac{M_w}{3} = \frac{158}{3} = 52.6]$$

c. In strongly basic medium:

Ionic equation:



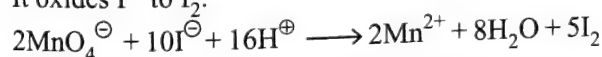
$$[E^\ominus \text{ of } \text{KMnO}_4 \text{ in strongly basic medium} = \frac{M_w}{1} = \frac{158}{1} = 158]$$

Note: It is clear that $[\text{H}^+]$ influences the reaction. But redox potential and kinetics of the reaction also are important factor. MnO_4^- at $[\text{H}^+] = 1$ should oxidise water (E^\ominus oxid for $\text{H}_2\text{O} = -1.23$ V) but in practice the reaction is extremely slow unless either Mn^{2+} ions are present or the temperature is raised.

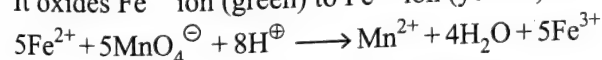
d. A few important oxidising reaction of KMnO_4 are given below in acid solutions.

The full ionic reaction is obtained by adding the half-reaction for MnO_4^- in different medium (acidic, basic and neutral) to the half-reaction of the reducing agent, balancing wherever necessary.

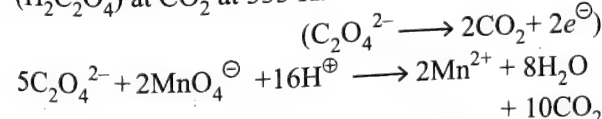
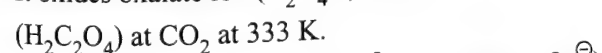
i. It oxidises I^- to I_2 .



ii. It oxidises Fe^{2+} ion (green) to Fe^{3+} ion (yellow)

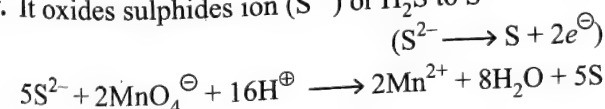


iii. It oxidises oxalate ion ($\text{C}_2\text{O}_4^{2-}$) or oxalic acid

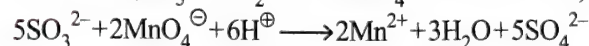
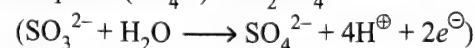


End point of reaction is from colourless to light pink.

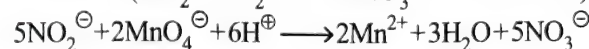
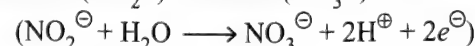
iv. It oxidises sulphides ion (S^{2-}) or H_2S to S



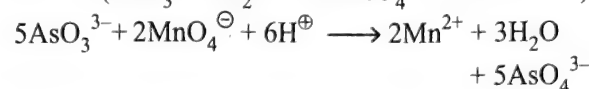
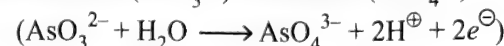
v. It oxidises sulphite ion (SO_3^{2-}) or sulphurous acid (H_2SO_3) to sulphate (SO_4^{2-}) or H_2SO_4 .



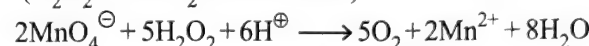
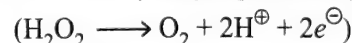
vi. It oxidises nitrite (NO_2^-) to nitrate (NO_3^-)



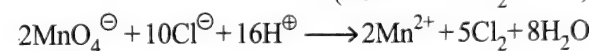
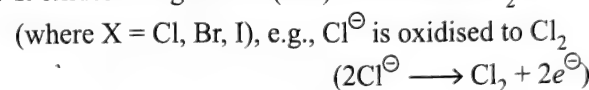
vii. It oxidises arsenite (AsO_3^{3-}) to arsenate (AsO_4^{3-})



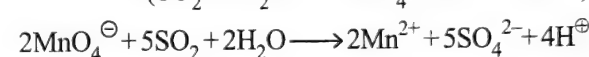
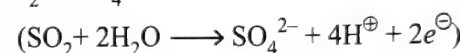
viii. It oxidises hydrogen peroxide (H_2O_2) to O_2



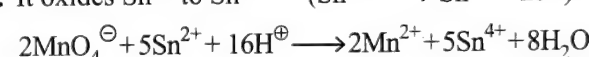
ix. It oxidises halogen acid (HX) or X^- ion to X_2



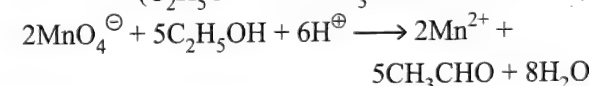
x. It oxidises SO_2 to SO_4^{2-}



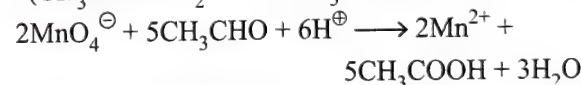
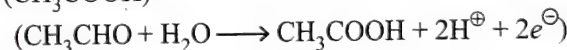
xi. It oxidises Sn^{2+} to Sn^{4+} ($\text{Sn}^{2+} \longrightarrow \text{Sn}^{4+} + 2e^-$)



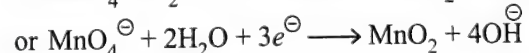
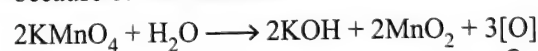
xii. It oxidises ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) to acetaldehyde (CH_3CHO)



xiii. It oxidises acetaldehyde (CH_3CHO) to acetic acid



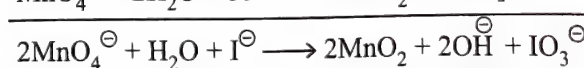
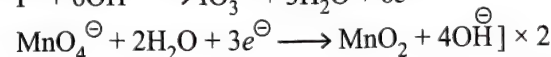
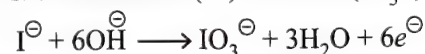
e. **In neutral or faintly alkaline solutions:** KMnO_4 acts as a moderate oxidising agent in neutral aqueous solution because of the reaction.



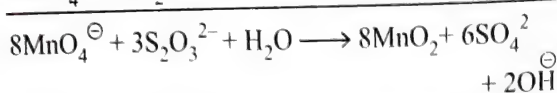
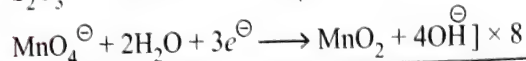
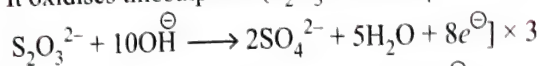
During the course of reaction, the alkali (OH^-) ions generated makes the medium alkaline even when the reaction is started in neutral medium.

Some oxidising properties of KMnO_4 in the neutral or faintly alkaline medium are given below:

i. It oxidises iodide (I^-) to iodate (IO_3^-)

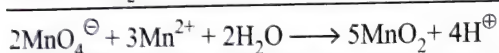
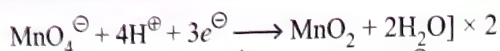


ii. It oxidises thiosulphate ($\text{S}_2\text{O}_3^{2-}$) to SO_4^{2-}

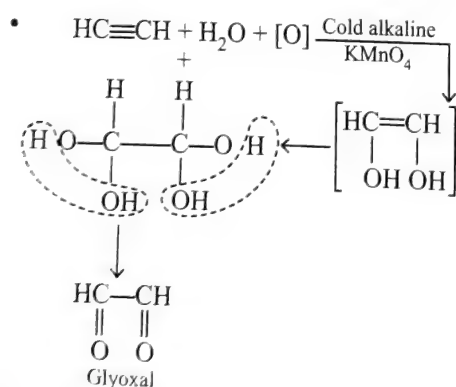
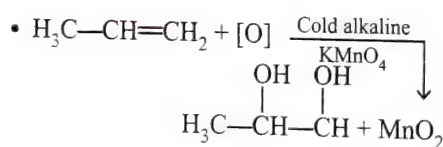
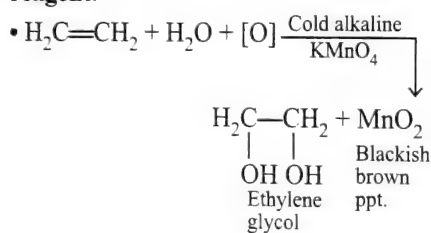


iii. It oxidises manganous (Mn^{2+}) salt to MnO_2 in neutral medium. The presence of ZnSO_4 or ZnO catalyses the oxidation.

Note: The ionic equation for the reduction of MnO_4^- in neutral medium is used



iv. It oxidises olefinic compounds to basic medium to glycols. The pink colour of KMnO_4 is discharged, and blackish brown precipitate of MnO_2 is obtained. This test is known as **Baeyer's test** for unsaturation and cold alkaline KMnO_4 is called **Baeyer's reagent**.



Note:

1. Titration of KMnO_4 in presence of HCl is unsatisfactory, since HCl is oxidised to Cl_2 .
 $(2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-)$

Moreover, the nascent oxygen produced from $\text{KMnO}_4 + \text{HCl}$ is partly used up to oxidise HCl to Cl_2 .

2. HNO_3 itself is an oxidising agent which reacts with reducing agents and therefore cannot be used in KMnO_4 in acidic medium.

3. H_2SO_4 is suitable for the titration of KMnO_4 in acidic medium, since it does not react with KMnO_4 or the reducing agent used. This is because SO_4^{2-} ion cannot be oxidised further since sulphur in SO_4^{2-} ion is present in its maximum oxidation state of +6. Moreover, H_2SO_4 does not give any nascent oxygen of its own to oxidise the reducing agent.

6.23.1 STRUCTURES OF MnO_4^- AND MnO_4^{2-}

1. Both MnO_4^- and MnO_4^{2-} are sp^3 hybridised and hence four O-atoms are arranged tetrahedrally around Mn atom as shown in Figure 6.10.

2. Purple MnO_4^- is diamagnetic and green MnO_4^{2-} is paramagnetic with one unpaired electron.

3. MnO_4^- is in +7 O.S. with $3d^0$ configuration and hence is diamagnetic, MnO_4^{2-} is in +6 oxidation state with $3d^1$ configuration and hence is paramagnetic.

4. The deep purple colour of KMnO_4 is not due to $d-d$ transition but due to charge transfer (from O to Mn) reducing the oxidation state of Mn from +7 to +6 momentarily. (LMCT, Ligand to metal charge transfer)

5. Both MnO_4^- and MnO_4^{2-} have $(p\pi-d\pi)$ multiple bonding. The bonding takes place by overlap of p -orbitals of O-atom with d -orbitals of Mn-atom.

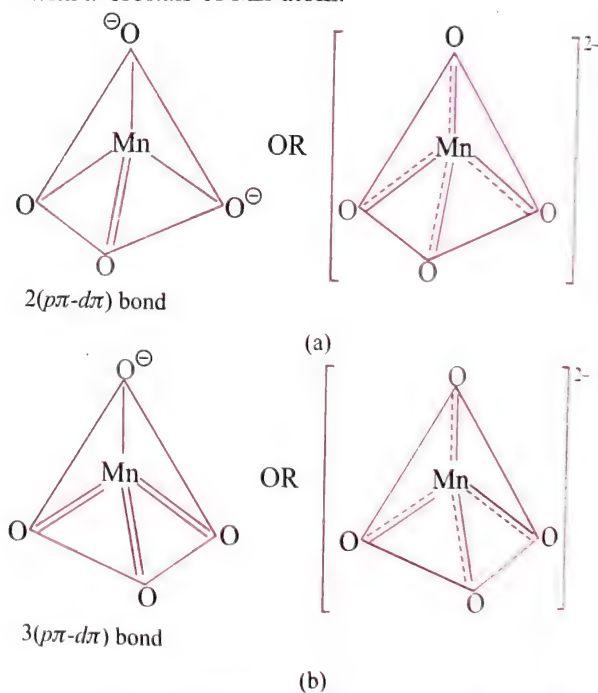


Fig. 6.10 (a) Tetrahedral structure of green MnO_4^{2-} ion and (b) Tetrahedral structure of purple MnO_4^- ion

Uses:

1. It is often used in volumetric analysis for the estimation of ferrous salts, oxalates, iodides and hydrogen peroxide.

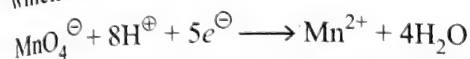
Note: It is not a primary standard because it is difficult to obtain it in the pure state and free from traces of MnO_2 . It is, therefore, always first standardised with a standard solution of oxalic acid.

2. It is used as a strong oxidising agent in the laboratory as well as in industry. It is a favourite and effective oxidising agent used in organic synthesis. Alkaline potassium permanganate is used for testing unsaturation in organic chemistry and is known as **Baeyer's reagent**.

3. Because of its strong oxidising power, it is also used for bleaching of wool, cotton, silk and other textile fibres and also for decolourisation of oils.

4. Potassium permanganate is also widely used as a disinfectant and germicide. A very dilute solution of permanganate is used for washing wounds and gargling for mouth sore. It is also used for purifying water of stinking wells.

5. **Use of KMnO_4 in redox-titrations:** KMnO_4 is a powerful and versatile oxidising agent and is widely used for titration against reducing agents like oxalic acid Mohr's salt. During the titration, the reduction of KMnO_4 by a reducing agent e.g., oxalic acid or Mohr's salt, produces manganous ions which are nearly colourless.



As the titration proceeds and when the whole of the reducing agent is consumed up, then the addition of an excess drop of KMnO_4 solution gives its own colour (pink) to the solution. Therefore, at the end point the colour changes from colourless to pink. Thus, KMnO_4 acts as a self-indicator.

6.24 THE INNER TRANSITION ELEMENTS (f-BLOCK) (OR) RARE EARTH ELEMENTS

6.24.1 GENERAL CHARACTERISTICS

The elements in which the last electron (also called differentiating electron) enter the antepenultimate energy level, i.e. $(n-2)$ orbitals are called **f-block elements**. These elements have also been called inner transition elements. This is because the last electron in them enters into $(n-2)$ f-orbitals, i.e., inner to the penultimate energy level and they form a transition series within the transition series (d-block elements). Their general electronic configuration is:

$$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$$

Thus, they have three incomplete shells, viz., $(n-2)$, $(n-1)$ and n th.

6.24.2 CLASSIFICATION OF f-BLOCK ELEMENTS

Depending upon whether the last electron enters a 4f-orbital or a 5f-orbital, the f-block elements have been divided into two series as follows:

1. **Lanthanoids:** The elements in which the last electron enters one of the 4f-orbitals are called 4f-block elements or first inner transition series. These are also called **lanthanides** or **lanthanons** or **lanthanoids** because they come immediately after lanthanum. Earlier, these 14 elements were called rare earth.

2. **Actinoids:** The elements in which the last electron enters one of the 5f-orbitals are called 5f-block elements or second inner transition series. These are also called **actinides** or **actinons** or **actinoids** because they come immediately after actinium.

3. Lanthanum, though a d-block element, is included in the lanthanoid series because it closely resembles lanthanoids for which the general symbol Ln is often used.

Similarly, actinium is also included in the actinoid series. Further the study of lanthanoids is comparatively easier because they show only one stable oxidation state. On the other hand, the chemistry of actinoids is much more complicated partly because they show a wide range of oxidation states and partly because they are radioactive.

4. They are also referred as rare earth elements, because their occurrence in earth is very rare. Cerium (Ce) constitutes about 3×10^{-4} % of earth's crust which is most commonly occurring lanthanoid.

5. The most common mineral containing lanthanoids is 'monazite sand'. It is mainly lanthanoid orthophosphate.

Table 6.13 Electronic configuration and radii of lanthanum and lanthanoids (Ln)

Atomic Number	Name	Symbol	Electronic configuration*				Oxidation states	Radii/pm	
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}		Ln	Ln^{3+}
57	Lanthanum	La	$5d^1 6s^2$	$5d^1$	$4f^0$		+3	187	106
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f^1$	$4f^0$	+3, +4	183	103
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$	$4f^1$	+3, +4	182	101
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	$4f^2$	+2, +3, +4	181	99
61	Promethium**	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$		+3	181	98
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$		+2, +3	180	96
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$		+2, +3	199	95
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1$	$4f^7$		+3	180	94
65	Terbium	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$	$4f^7$	+3, +4	178	92
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$	$4f^8$	+3, +4	177	91
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{11}$	$4f^{10}$		+3	176	89
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{12}$	$4f^{11}$		+3	175	88
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{13}$	$4f^{12}$		+2, +3	174	87
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{14}$	$4f^{13}$		+2, +3	173	86
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1$	$4f^{14}$		+3	—	—

*Only electrons outside [Xe] core are indicated.

**Promethium is the only synthetic (man made) radioactive lanthanoid

Note: Elements with $4f^2$ and $4f^8$ electronic configuration are not known.

Note:

1. From the electronic configuration of Ln given in Table, it is clear that electron can shift between f- and d-orbitals depending upon the stability of electronic configuration.
2. As we move higher in energy levels, energy gap is decreasing and shifting of electron is very much possible.

6.24.3 ATOMIC AND IONIC SIZES

There is gradual steady decrease in atomic/ionic radii along the lanthanoid series from La to Lu and La^{3+} to Lu^{3+} . This regular decrease in the sizes of the atoms and ion with increasing atomic number is called **lanthanoid contraction** (Figure 6.11).

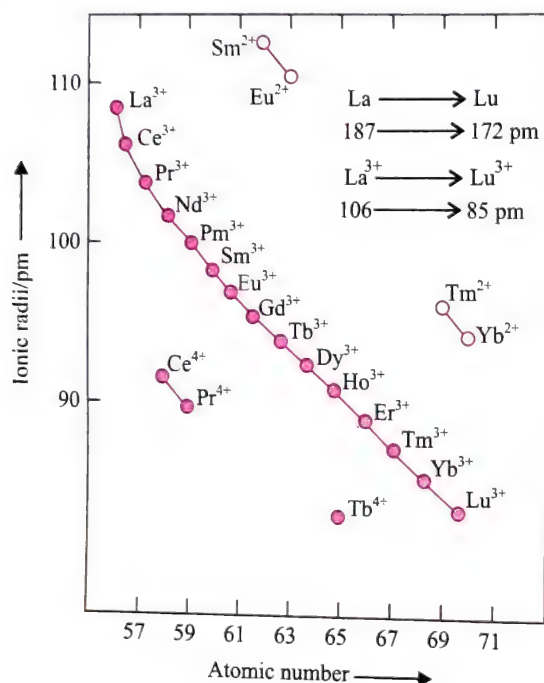


Fig. 6.11 Trends in ionic radii of lanthanoids

Explanation: The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanoid contraction). It has far reaching consequences in the chemistry of the third transition series of the elements. The decrease in atomic radii is not quite regular as it is regular in M^{3+} ions. This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same causing the imperfect shielding of one electron by another in the same sub-shell. However, the shielding of one 4f electron by another is less than one d electron by another. Hence with the increase in nuclear charge along the series, there is fairly regular decrease in the sizes with increasing atomic number.

The cumulative effect of the contraction of lanthanoid series, known as lanthanoid contraction, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm) a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

6.24.4 CONSEQUENCES OF LANTHANOID CONTRACTION

1. **Difficulty in separation of lanthanoids:** Since the change in ionic radii (size of the ions) in lanthanides is very small, their chemical properties are similar. This makes the separation of the elements in the pure state difficult. However, lanthanide contraction results in slight difference in the size of lanthanides which results in the differences in properties like solubility, complex ion formation, hydration etc. These differences enable the separation of individual lanthanide elements by (i) **valency change** and (ii) **ion exchange chromatographic methods by using zeolites**.

i. **Valency change:** A few lanthanides have oxidation states of +4 or +2. The properties of Ln^{4+} or Ln^{2+} are so different from those of Ln^{3+} that separation is fairly easy.

Ce can be separated from lanthanide mixtures quite easily as it is the only lanthanide which has Ln^{4+} ions stable in aqueous solution.

Oxidising a solution containing a mixture of Ln^{3+} ions with NaOCl under alkaline conditions produces Ce^{4+} . Because of the higher charge, Ce^{4+} is much smaller and less basic than Ce^{3+} or any other Ln^{3+} . The Ce^{4+} is separated by carefully controlled precipitation of CeO_2 or $\text{Ce}(\text{IO}_3)_4$, leaving the trivalent ions in solution.

Alternatively Ce^{4+} can readily be extracted from other Ln^{3+} lanthanides by solvent extraction in HNO_3 solution using tributyl phosphate. Ninety-nine per cent pure Ce can be obtained in one stage from a mixture containing 40% Ce.

Valency change is still useful method for purifying Ce and Eu despite the advent in recent years of ion exchange.

- ii. **Ion exchange chromatographic methods by using zeolites:** Ion exchange method is based on the fact that hydrated radii of lanthanoid ions increase with increasing atomic number. Thus, when a solution containing several lanthanoid ions passes slowly through the column of cation exchange resin, the heavier members will come through first.
2. **Similarity in size of elements belonging to same group of second and third transition series:** In general, the size of the atoms increases down a group (\downarrow). However, whereas the size of the atom of any element lying in the second transition series is larger than that of the atom of the element lying in the same group of the transition series (as expected), the size of any atom of the third transition series (after lanthanum) is nearly same as that of the atom of the element lying in the same group of the second transition series. A few elements of the 1st, 2nd and 3rd transition series along with their covalent radii are given in Table 6.14.

The similarity in size of the atoms of the elements belonging to the same group of the 2nd and 3rd transition series (after lanthanum) (e.g. $r_{\text{Zr}} \approx r_{\text{Hf}}$ and $r_{\text{Nb}} \approx r_{\text{Ta}}$) is evidently due to the effect of lanthanide contraction.

Table 6.14 Covalent radii of some transition elements

Group No.	3	4	5	6
3d series	Sc (21) 144 pm	Ti (22) 132 pm	V (23) 122 pm	Cr (24) 117 pm
4d series	Y (39) 162 pm	Zr (40) 145 pm	Nb (41) 134 pm	Mo (42) 129 pm
5d series	La (57) 169 pm	Hf (72) 144 pm	Ta (73) 134 pm	W (74) 130 pm

14 Lanthanide elements (58–71)

3. **Effect on the basic strength of hydroxides:** As the size of the lanthanide ions decreases from La^{3+} to Lu^{3+} , the covalent character of the hydroxides increases and hence the basic strength decreases (**Fajan's rule**). Thus $\text{La}(\text{OH})_3$ is most basic whereas $\text{Lu}(\text{OH})_3$ is least basic.

6.24.5 OXIDATION STATE

- The most predominant and stable oxidation state (O.S.) of lanthanoids is +3.
- However, +2 and +4 ions in solution and solid compounds also exist.
- Like irregularity in I.E., the irregularity in O.S. arises mainly from the stable electronic configuration of half-filled or fully filled 4f-orbitals, for example Eu^{2+} ($4f^7$), Yb^{2+} ($4f^{14}$), Ce^{4+} ($4f^0$) and Tb^{4+} ($4f^7$)

Note: Lanthanoids show limited number of O.S. because there is a large energy gap between 4f and 5d subshells.

- Both +2 and +4 O.S. have a tendency to revert back to more stable O.S. of +3.
- $E^\ominus_{\text{Ce}^{4+}/\text{Ce}^{3+}} = +1.74 \text{ V}$, which suggests that it can oxidise water, still it is used as an *oxidising agent* in analytical chemistry because the oxidation of H_2O by Ce^{4+} is kinetically a very slow process.
- Pr, Nd, Tb and Dy also exhibit +4 O.S. but only in oxides, MO_2 .
- Eu^{2+} and Yb^{2+} have a tendency to undergo oxidation to +3 O.S. and hence acts as *reducing agent* in aqueous solutions.
- Likewise Ce^{4+} and Tb^{4+} have a tendency to undergo reduction to +3 O.S. and hence acts as *oxidising agent*.
- Like Eu, Sm exhibits both +2 and +3 O.S.
- Exceptions:** As shown in Table 6.13, some elements show an O.S. of +2 and +4, even though their ions do not have f^0, f^7 or f^{14} configuration, e.g., Pr^{4+} ($4f^1$), Nd^{2+} ($4f^4$), Nd^{4+} ($4f^2$), Sm^{2+} ($4f^6$), Dy^{4+} ($4f^8$) etc.

6.24.6 PHYSICAL PROPERTIES

- All the lanthanoids are silvery white soft metals and tarnish rapidly in the air. Their hardness increases with increasing atomic number. Samarium (Sm) is exceptionally hard like steel.
- All of them have typical metallic structure and are good conductors of heat and electricity.
- They have high densities which lie in the range from 6.77 to 9.74 g cm^{-3} . Density and other properties vary smoothly

with increasing atomic number except for Eu and Yb and occasionally for Sm and Tm.

- They have high melting points in the range from 1000 to 1200 K except samarium which has a very high melting point of 1623 K.
- La^{3+} (f^0), Ce^{4+} ($4f^0$) and Lu^{3+} ($4f^{14}$) configuration have no unpaired electrons and are diamagnetic. All other 4f elements / ions contain unpaired electrons and are therefore paramagnetic.
- Lanthanoids differ from transition elements in the fact that their magnetic moments do not obey 'spin only' formula, viz., $\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ BM}$, where n is the number of unpaired electrons. **This is because in case of transition elements, the orbital contribution is quenched by the electric field of the environment but in case of lanthanoids, 4f orbitals are much more penetrated towards nucleus than 'd' orbitals therefore orbital contribution is not ignored.** Hence, their magnetic moment is calculated by considering spin as well as orbital contribution, i.e.,

$$\mu_{(S+L)} = \sqrt{4S(S+1) + L(L+1)} \text{ BM}$$

where S is spin quantum number and L is orbital quantum number.

The magnetic moment calculated by spin only formula works with La^{3+} (f^0), Gd^{3+} (f^7) and Lu^{3+} (f^{14}). La^{3+} and Lu^{3+} have no unpaired electrons ($n = 0$) therefore $\mu_s = 0$. Gd^{3+} have 7 unpaired electrons ($n = 7$) and

$$\mu_s = \sqrt{7(7+2)} = \sqrt{63} = 7.9 \text{ BM}$$

The other lanthanide ions do not obey the simple relationship.

The 4f electrons are well shielded from external fields by the overlying 5s and 5p electrons. Thus the magnetic effect of the motion of the electron in its orbital is not quenched out. Thus the magnetic moments must be calculated taking into account both the magnetic moment from the unpaired electron spins and that from the orbital motion. This also happens with the second and third row transition elements. However, the magnetic properties of the lanthanides are fundamentally different from those of the transition elements. In the lanthanides the spin contribution S and orbital contribution L couple together to give a new quantum number J .

$$J = L - S \text{ when the shell is less than half full}$$

$$\text{and } J = L + S \text{ when the shell is more than half full}$$

The magnetic moment μ is calculated in Bohr magnetons (BM) by

$$\mu = g\sqrt{J(J+1)} \text{ where } g = 1\frac{1}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Figure 6.12 shows the calculated magnetic moments for the lanthanide ions in +3 O.S. momentum formula using both the simple spin only formula and the coupled spin plus orbital momentum formula.

The unusual shape of the spin plus orbital motion curve arises because of Hund's third rule. When the f level is less than half full the spin and orbital momenta contributions

work in opposition ($J = L - S$). When the f shell is more than half full they work together ($J = L + S$).

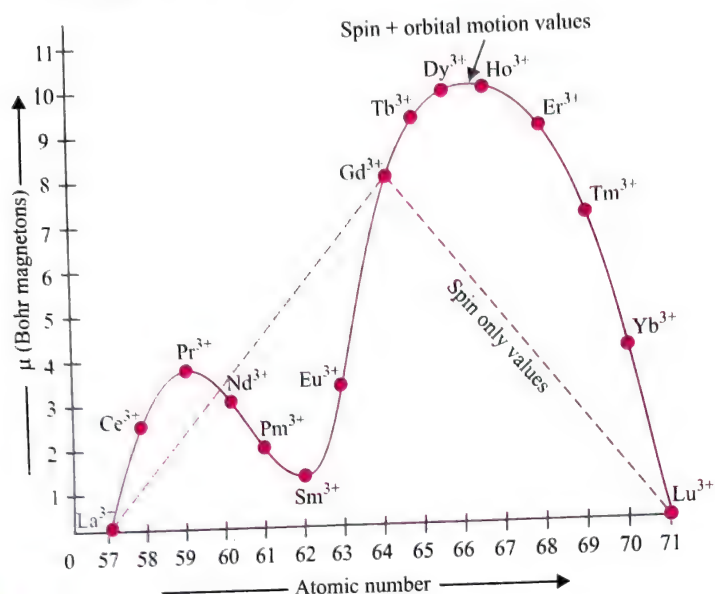


Fig. 6.12 Paramagnetic moments of Ln^{3+} lanthanide ions at 300 K. Spin only values are shown as a broken line, and the spin plus orbital motion as solid lines

The calculated and observed magnetic moment values of La^{3+} and Ln^{3+} ions are given in Table.

Table 6.15 Magnetic moments of La^{3+} and Ln^{3+} ions

Symbol and atomic number	Electronic structure of Ln^{3+}	Magnetic moment (BM)	
		Calculated	Observed
La (57)	$4f^0$	0	0
Ce (58)	$4f^1$	2.54	2.3-2.5
Pr (59)	$4f^2$	3.58	3.4-3.6
Nd (60)	$4f^3$	3.62	3.5-3.6
Pm (61)	$4f^4$	2.68	2.7
Sm (62)	$4f^5$	0.84	1.5-1.6
Eu (63)	$4f^6$	0	3.4-3.6
Gd (64)	$4f^7$	7.94	7.8-8.0
Tb (65)	$4f^8$	9.72	9.4-9.6
Dy (66)	$4f^9$	10.63	10.4-10.5
Ho (67)	$4f^{10}$	10.60	10.3-10.5
Er (68)	$4f^{11}$	9.57	9.4-9.6
Tm (69)	$4f^{12}$	7.63	7.1-7.4
Yb (70)	$4f^{13}$	4.50	4.4-4.9
Lu (71)	$4f^{14}$	0	0

7. The lanthanoids are silvery white metals. However, most of the trivalent metal ions are coloured, both in the solid state and in aqueous solution. This is due to the partly filled f -orbitals which permit $f-f$ transition.

La^{3+} ($4f^0$), Ce^{4+} ($4f^0$), Lu^{3+} ($4f^{14}$) and Yb^{2+} ($4f^{14}$) are colourless because of no $f-f$ transitions is possible, but the rest do so. However, absorption bands are narrow because of the excitation within f -levels.

Lanthanoid ions with $n f$ electrons have a similar colour to those with $(14 - n) f$ electrons, e.g., La^{3+} and Lu^{3+} are colourless, Sm^{3+} and Dy^{3+} are yellow and Eu^{3+} and Tb^{3+} are pink.

8. IE_1 of lanthanoids are around 600 kJ mol^{-1} and the $\text{IE}_2 \approx 1200 \text{ kJ mol}^{-1}$ which are comparable with those of Ca. The variation of the IE_3 shows that just as in case of $3d$ transition series, the loss of the first two electrons is accompanied by exchange enthalpy. Further, the loss of third electron is easier, i.e., IE_3 is low if it leads to stable empty, half-filled or completely filled configuration, as indicated by the abnormally low IE_3 values of La, Gd and Lu.
9. Their standard reduction potentials, i.e., $E^\ominus_{\text{M}^{3+}(\text{aq})/\text{M}(\text{s})}$ values for the half reaction lie in the range from -2.2 to -2.4 V , the only exception being europium (Eu) for which the E^\ominus value is -2.0 V .
10. They are highly electropositive because of their low ionisation enthalpies.
11. They readily lose electrons and are thus good reducing agents.
12. They do not have much tendency to form complexes due to low charge density because of their large size. The tendency to form complexes and their stability increases with increasing atomic number.

6.24.7 CHEMICAL PROPERTIES

The first few members of the series are quite reactive, almost like calcium. However, with increasing atomic number, their behaviour becomes similar to that of aluminium.

1. They combine with H_2 on gentle heating.
2. When heated with carbon, they form carbides, e.g., Ln_2C_3 and LnC_2 .
3. They burn in halogens to form halides.
4. They react with dilute acids to liberate H_2 gas.
5. They form oxides and hydroxides of the type M_2O_3 and $\text{M}(\text{OH})_3$ which are basic like alkaline earth metal oxides and hydroxides. The hydroxides are definite compounds not just hydrated oxides.

The general reactions are shown in Figure 6.13.

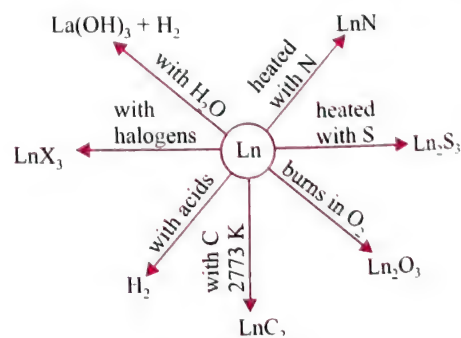


Fig. 6.13 Chemical reactions of the lanthanoids

6.24.8 USES OF LANTHANIDS

1. Lanthanoids are used in the production of alloy steels to improve the strength and workability of steel. A well known alloy is **mischmetal** which has the following composition.

Name of the alloys	Composition
Mischmetal	Lanthanoid metals = 95% (about 40% La, 50% Ce and the rest other lanthanoids) Iron = 5% S, C, Ca and Al = traces

The maximum amount of mischemetal is used in making a magnesium-based alloy (i.e., Mg mixed with about 3% **mischmetal** to increase the strength of Mg). It is called **pyrophoric alloy**.

Name of the alloys	Composition
Pyrophoric alloy: They are used in making bullets, shells and lighter flints (because it emits spark when struck)	Ce = 45.5% La + Nd = 44% Fe = 4.5% Al = 0.5% Ca, Si and C = traces

- Because of their paramagnetic and ferromagnetic properties, their compounds are used in making magnetic and electronic devices.
- Their oxides e.g., La_2O_3 are used as phosphor for television screens and similar fluorescing surfaces.
Mixed oxides of lanthanoids are used as catalysts in petroleum cracking.

ILLUSTRATION 6.14

Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

Sol. Cerium ($Z = 58$)

6.25 ACTINOIDS

- The actinoids include 14 elements from the (thorium) to Lr (lawrencium). The names, symbols, valence electronic configuration and some properties are given in Table.

Table 6.16 Some properties of actinium and actinoids

Atomic Number	Name	Symbol	Electronic configuration*				Radii/pm	
			M	M ³⁺	M ⁴⁺	M ⁴⁺	M ³⁺	M ⁴⁺
89	Actinium	Ac	$6d^1 7s^2$	$5d^0$	$4f^0$		111	
90	Thorium	Th	$6d^2 7s^2$	$5f^1$	$4f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	$4f^2$	$5f^1$		96
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	$4f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	$4f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	$4f^5$	$5f^4$	100	90
95	Americium	Am	$5f^7 7s^2$	$5f^6$	$4f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	$4f^7$	$5f^6$	99	88
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	$4f^8$	$4f^7$	98	87
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	$4f^9$	$4f^8$	98	86
99	Einsteinium	Es	$5f^{11} 7s^2$	$5f^{10}$	$4f^{10}$	$5f^9$	—	—
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	$4f^{11}$	$5f^{10}$	—	—
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	$4f^{12}$	$5f^{11}$	—	—
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	$4f^{13}$	$5f^{12}$	—	—
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	$4f^{14}$	$5f^{13}$	—	—

Note: Elements with $5f^1$, $5f^5$ and $5f^8$ electronic configuration are not known.

- The actinoids are radioactive elements. The earlier members have relatively long half lives, ranging from a day to 3 minutes for Lr ($Z = 103$). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

6.25.1 GENERAL ELECTRONIC CONFIGURATION



- All the actinoids have common $7s^2$ configuration and variable occupancy of $5f$ and $6d$ subshells.
- The 14 electrons are being added into $5f$, except in Th ($Z = 90$) but filling of $5f$ continues again after Th till $5f$ orbitals are complete Lr ($Z = 103$).

- The irregularities in the electronic configurations of actinoids like those in the lanthanoids are related to the stabilities of f^0 , f^7 and f^{14} configurations, for example, the configuration of Am and Cm are $5f^7 6d^0 7s^2$ and $5f^7 6d^1 7s^2$ respectively.
- Berkelium (Bk, $Z = 97$) also shows an exceptional configuration of $5d^0 6d^0 7s^2$ which is neither half-filled nor completely filled.

6.25.2 IONIC SIZES

Like lanthanoids, there is a gradual decrease in the size of atoms or M^{3+} ions across the series (Table). This is called **actinoid contraction** (like lanthanoid contraction) attributed to poor

shielding effect of the 5f-electrons, which results in the decrease of size of M/M^{3+} .

This contraction is greater from element to element in this series resulting from poor shielding by 5f-electrons.

Moreover, poor shielding effect of 5f-orbital than 4f-orbitals is also due to less penetration effect of 5f-orbitals than 4f-orbitals.

6.25.3 OXIDATION STATES OF ACTINIDS

1. Unlike lanthanoids, actinoids show a large number of oxidation states.

Table 6.17 Oxidation states (O.S.) of actinium and actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3	(3)	3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	(4)	(4)	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

Note: O.S. given in brackets are less stable.

This is because of very small energy gap between 5f, 6d and 7s subshells. Hence, all their electrons can take part in bond formation.

2. The dominant oxidation state of these elements is 3 (similar to lanthanoids). Besides +3 state, actinoids also exhibit an oxidation state of +4. Some actinoids show still higher oxidation states.
3. The maximum oxidation state first increases up to the middle of the series and then decreases, e.g., it increases from +4 for Th to +5, +6 and +7 for Pa, U and Np but decreases in the succeeding elements.
4. The actinoids resemble lanthanoids in having more compounds in +3 state than in the +4 state.
However, the compounds in the +3 and +4 state tend to undergo hydrolysis.
5. Both 5f and 4f orbitals have similar shapes and they resemble in their angular part of the wave functions. But 4f orbitals are much more penetrated (or more buried) than 5f orbital towards nucleus. Hence 5f electrons can participate in bond formation to a far greater extent. That is why actinoids have low IE and more reactive than lanthanoids.

6.25.4 PHYSICAL PROPERTIES

1. Like lanthanoids, actinoids are metals with silvery appearance.
2. The actinoids like lanthanoids have high melting and boiling points. However, they do not show any regular trend with rise in atomic number.
3. **Density:** All the actinoids except Th and Am have high densities.
4. The actinoids have lower ionisation enthalpies than lanthanoids because 5f is less penetrating than 4f and hence is more effectively shielded from the nuclear charge.

5. These metals are silvery white. However, actinoid cations are generally coloured. The colour of the cation depends upon the number of 5f-electrons. The cations containing no 5f-electron or having seven 5f-electrons (i.e., exactly half-filled f-subshell) are colourless. The cations containing 2 to 6 electrons in the 5f-subshell are coloured both in the crystalline state as well as in aqueous solution. The colour arises due to f-f transition e.g. Ac^{3+} ($5f^0$) = colourless, U^{3+} ($5f^3$) = Red, Np^{3+} ($5f^4$) = Blue, Pu^{3+} ($5f^5$) = Violet, Am^{3+} ($5f^6$) = Pink, Cm^{3+} ($5f^7$) = Colourless, Th^{3+} ($5f^0$) = Colourless and so on.

6. As they have much greater irregularities in their metallic radii than lanthanoids, they show great structural variability.
7. **Electropositive character:** All the known actinoid metals are highly electropositive. They resemble the elements of lanthanoid series in this respect.
8. **Magnetic behaviour:** Like lanthanoids, the actinoid elements are strongly paramagnetic.

The variation in magnetic susceptibility of actinoids with the increasing number of unpaired electrons is similar to that of lanthanoids but the values are higher for the actinoids than the lanthanoids.

9. **Reducing agents:** All the actinoids are strong reducing agents.

6.25.5 CHEMICAL PROPERTIES

1. They are highly reactive metals especially in the finely divided state.
2. All these metals are attacked by hydrochloric acid but the effect of nitric acid is very small due to the formation of a protective oxide layer on their surface.
3. Alkalines have no action on them.
4. They combine with most of the non-metals at moderate temperature.
5. They react with boiling water to give a mixture of oxide and hydride.

6.25.6 USES OF ACTINIDS

The three most important actinoids which find uses as such or in the form of their compounds are Th, U and Pu.

1. Th is used in atomic reactors and in the treatment of cancer. Its salts are used in making incandescent gas mantles.
2. U is used as nuclear fuel. Its salts are used in glass industry (for imparting green colour), textile industry, ceramic industry and in medicines.
3. Pu is used as fuel for atomic reactors as well as for making atomic bombs.

6.25.7 COMPARISON OF LANTHANIDS AND ACTINIDS

1. Both show mainly an oxidation state of +3.
2. Both are electropositive and very reactive.
3. Both exhibit magnetic and spectral properties.

4. Actinoids exhibit actinoid contraction like lanthanoid contraction shown by lanthanoids.

Difference: Some differences in their properties are shown as:

Lanthanoids	Actinoids
i. Besides +3 oxidation state, they show +2 and +4 oxidation states only in few cases.	i. Besides +3 oxidation state, they show higher states of +4, +5, +6, +7 also.
ii. Lanthanoid compounds are less basic.	ii. Actinoid compounds are more basic.
iii. They have less tendency towards complex formation.	iii. They have greater tendency towards complex formation.
iv. Most of their ions are colourless.	iv. Most of their ions are coloured.
v. Except promethium, they are non-radioactive.	v. They are radioactive.
vi. Their magnetic properties can be explained easily.	vi. Their magnetic properties cannot be explained easily, as they are more complex.

6.26 SOME APPLICATIONS OF d- AND f-BLOCK ELEMENTS

1. Iron and steel (important construction materials) are produced by the reduction of iron oxides. Cr, Mn and Ni are used as alloying metals.

2. TiO is used in white pigment.

3. MnO₂ is used in dry battery cells.

4. Zn and Ni/Cd are also used in battery industry.

5. Coinage metals (group 11 elements), Cu, Ag, Au are used as collection items.

UK copper coins are copper-coated steel. 'silver' UK coins are Cu/Ni alloy.

6. V₂O₅ is used as catalyst in the manufacture of H₂SO₄ by contact process.

7. Fe is used as catalyst in the Haber process for the production of NH₃ from N₂/H₂ mixtures.

8. Ni is used as catalyst for the hydrogenation of oils.

9. In the Wacker process the oxidation of ethyne to ethanal is catalysed by PdCl₂.

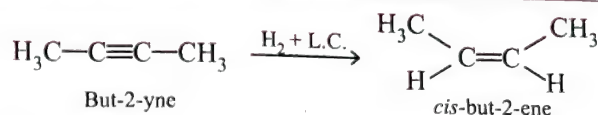
10. Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene.

11. The photographic industry relies on the special light sensitive properties of AgBr.

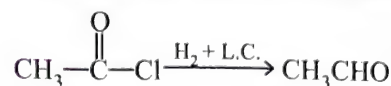
12. Triethyl aluminium [(C₂H₅)₃Al] and TiCl₄ form the basis of Ziegler-Natta type heterogeneous catalyst is used as a catalyst for the low temperature polymerisation of alkenes (i.e. for the synthesis of high density polythene (HDPE) from ethene.

13. Homogeneous Wilkinson's catalyst [RhCl(Ph₃P)₃] is used as a catalyst in the hydrogenation of alkenes.

14. Lindlar's catalyst (LC) (Pd + BaSO₄ + S or quinoline in boiling xylene). It is also called poisoned palladium. It is used in the hydrogenation of alkyne to *cis* alkene e.g.,

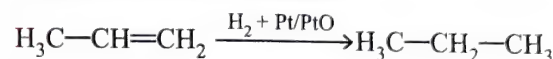


It is also used to convert acid halides (RCOX) to aldehydes and the reaction is known as Rosenmund reduction, e.g.



15. P-2 or brown catalyst. It is nickel boride (Ni₂B). It is also used in the hydrogenation of alkyne to *cis* alkene.

16. Adam's catalyst (Pt/PtO): It is also used for the hydrogenation of alkene to alkane.



17. Finely divided Pt is a black powder and is called platinum black. Finely divided Ag is also black in colour.

18. 1st triad of group VIII (8, 9, 10 group) Fe, Co and Ni collectively are called coinage metals. They are ferromagnetic.

19. 2nd and 3rd triads of group VIII (8, 9, 10 group), Ru, Rh and Pd (2nd triad), Os, Ir and Pt (3rd triad), collectively are called platinum metals.

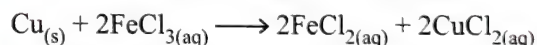
ILLUSTRATION 6.15

- a. A strip of Cu dissolves in FeCl₃, however Cu cannot displace Fe.

- b. [CuCl₄]²⁻ exists but [CuI₄]²⁻ does not. Why?

Sol.

- a. This is because $E^\ominus_{\text{Fe}^{3+}/\text{Fe}^{2+}} > E^\ominus_{\text{Cu}^{2+}/\text{Cu}}$



This method is used for making printed circuit boards (PCB's) used in electronic industry.

- b. I[⊖] ion is a stronger reducing agent than Cl[⊖] ion, therefore I[⊖] ion reduces Cu²⁺ to Cu[⊕] ion. As a result CuI₂ is converted into CuI and hence [CuI₄]²⁻ does not exist.

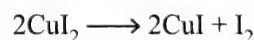


ILLUSTRATION 6.16

- a. Why Mn²⁺ compounds are more stable than Fe²⁺ towards oxidation to their +3 state?

- b. Calculate the magnetic moment of V³⁺ ion.

- c. [Ti(H₂O)₆]³⁺ gives violet coloured aqueous solution but [Mg(H₂O)₆]²⁺ solution is colourless.

- d. [Ti(H₂O)₆]³⁺ is coloured whereas [Sc(H₂O)₆]³⁺ is colourless. Why?

Sol.

- a. Electronic configuration of Mn²⁺ is 3d⁵ which is half-filled and hence stable. Therefore IF₃ is very high i.e. 3rd electron cannot be lost easily. In case of Fe²⁺, electronic configuration is 3d⁶. Hence it can lose one electron easily to give the stable configuration 3d⁵.

b. $V(Z = 23) \Rightarrow 3d^3 4s^2$, $V^{3+} = 3d^2$ ($n = 2$)

$$\mu = \sqrt{n(n+2)} \text{ BM} = \sqrt{2(2+2)} = \sqrt{8} = 2.73 \text{ BM}$$

- c. In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, the d^1 electron occupies t_{2g} orbital in octahedral field. On irradiation with light, the t_{2g} electron is promoted to e_g orbital and the resulting absorption band gives violet colour.

In case of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ the electronic configuration of Mg^{2+} is $1s^2, 2s^2, 2p^6$ which does not permit any electronic transition ($2p \rightarrow 3s$) as the energy gap is very large or there does not occur $d-d$ transition of electron. Hence, it gives colourless solution.

- d. A In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, the titanium ion is present in Ti^{3+} form with $3d^1, 4s^0$ configuration. The single unpaired electron of $3d^1$ orbital makes the compound to show colour. In $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$, scandium is present as Sc^{3+} state with $3d^0 4s^0$ configuration. Since no electron is present in the $3d$ and $4s$ orbitals, it remains colourless.

ILLUSTRATION 6.17

- Why Sm^{2+} , Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents but an aqueous solution of Ce^{4+} is a good oxidising agent?
- Why does $\text{Mn}(\text{II})$ show maximum paramagnetic character amongst the bivalent ions of the first transition series?
- $\text{La}(\text{OH})_3$ is more basic than $\text{Lu}(\text{OH})_3$. Explain. (Atomic no. of La = 57, Lu = 71)
- Give reason. Why in moist air copper corrodes to produce a green layer on the surface.
- Which of the following ions are expected to be coloured and why? Fe^{2+} , Mn^{2+} , Cr^{3+} .
- Why Zn^{2+} salts are white while Ni^{2+} salts are blue?

Sol.

- The most stable oxidation state of lanthanides is +3 hence ions in +2 state tend to change to +3 state by loss of electron and those in +4 state tend to change to +3 state by gain of electron.
- Mn^{2+} has maximum number of unpaired electrons.
- As the size of lanthanide ions decreases from La^{3+} to Lu^{3+} , the covalent character of the hydroxides increases. Hence the basic strength decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$.
- Copper in presence of moisture oxygen and carbon dioxide of atmosphere is converted into basic carbonate which is deposited as green layer on surface.

$$2\text{Cu} + \text{CO}_2 + \text{H}_2\text{O} + \text{O}_2 \longrightarrow \text{Cu}(\text{OH})_2\text{CuCO}_3$$
- Fe^{2+} , Mn^{2+} , Cr^{3+} are coloured due to $d-d$ transition of electron takes place.
- Zn^{2+} has completely filled d -orbitals ($3d^{10}$) while Ni^{2+} has incompletely filled d -orbitals ($3d^8$).

CONCEPT APPLICATION EXERCISE 6.1

- Explain why Mn^{3+} is less stable than Mn^{2+} and Mn^{4+} ions?
 or
 Explain why Mn^{3+} disproportionate into Mn^{2+} and Mn^{4+}
 - Standard reduction potential of copper is greater than that of hydrogen yet it liberates hydrogen from a concentrated solution of hydrochloric acid. Explain this fact with proper reasoning.

$$\text{Cu}^{2+} + 2e \longrightarrow \text{Cu}_{(s)} \quad E_{\text{Cu}^{2+}/\text{Cu}}^\ominus = 0.34 \text{ volt}$$

$$2\text{H}^\oplus + 2e \longrightarrow \text{H}_{2(g)} \quad E_{\text{H}^\oplus/\text{H}_2}^\ominus = 0.00 \text{ volt}$$
 - An aqueous solution of FeCl_3 is slightly yellowish in colour.
 - $\text{Cu}(\text{I})$ compounds are not known in aqueous solution.
- Write down the names of crystal structures in which the following elements are present:
 Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn
 - Which is more basic?
 i. ZrO_2 or TiO_2 ii. V_2O_5 or Nb_2O_5 iii. OsO_4 or ReO_2
 - Which is more oxidising agent $\text{Cr}(\text{VI})$ or $\text{Mo}(\text{VI})$?
- Write down the name of catalyst for the following:
 - In the synthesis of hydrocarbon in Fischer-Tropsch process.
 - Adams catalyst in reduction.
 - Deacon's process of making Cl_2 from HCl .
 - Reppé synthesis of benzene.
 - Fenton's reagent in the synthesis of aldehydes from alcohols.
- Arrange the following complexes in decreasing order of magnetic moment:
 $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$
 - Give the formula of three ions which are coloured due to charge transfer spectra.
- What happen when:
 - CO_2 gas is passed through aqueous solution of Na_2CrO_4 .
 - Ammonium dichromate is heated strongly.
 - Two gases 'A' and 'B' turns acidified $\text{K}_2\text{Cr}_2\text{O}_7$ green. When these gases are passed through water simultaneously, solution turns turbid yellow. What are the gases 'A' and 'B'?
- Explain by giving suitable reason.
 - Yellow coloured aqueous solution of sodium chromate changes to orange-red when CO_2 under pressure is passed.
 - Green solution of potassium manganate, K_2MnO_4 turns purple when CO_2 is circulated.
 - Hg^{2+} and Hg_2^{2+} salts are colourless.
 - Cu^{2+} salts are paramagnetic while Cu^\oplus salts are diamagnetic in nature.
- Explain:
 - Why is $\text{K}_2\text{Cr}_2\text{O}_7$ generally preferred to $\text{Na}_2\text{Cr}_2\text{O}_7$ in volumetric analysis?

- b. Which divalent metal ion has maximum paramagnetic character among the first transition metals? Why?
- c. How the colour of $K_2Cr_2O_7$ solution does depend on pH of the solution?
8. a. Why do second and third rows of transition elements resemble each other more closely than the first row? Give reasons:
- b. Most transition metals show paramagnetic behaviours.
- c. Transition metal and their many compounds are coloured.
9. Acidified $K_2Cr_2O_7$ solution turns green when sodium sulphite is added to it. Explain.
10. Identify A, B, C, D and X.
When a white crystalline compound X is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4 , a reddish brown gas A is evolved. On passing A into caustic soda solution, a yellow coloured solution of B is obtained. Neutralising the solution of B with acetic acid and on subsequent addition of lead acetate, a yellow precipitate C is obtained. When X is heated with NaOH solution, a colourless gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish brown precipitate D is formed.
11. Complete and balance the following equations:
- $K_2Cr_2O_7 + \dots + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$
 - $K_2Cr_2O_7 \xrightarrow{400^\circ C} \Delta$
 - $KMnO_4 \xrightarrow{200^\circ C} \Delta$
 - $MnO_4^- + AsO_3^- + H^+ \longrightarrow$
 - $K_2Cr_2O_7 + \xrightarrow{NH_4Cl} \xrightarrow{\Delta} (Gas) + (Green)$
(Metal) + (Oxide) $\xleftarrow{\Delta} Al$
12. Explain the following giving suitable reason:
- Transition metals of 3d-series do not react readily with dilute acids to liberate hydrogen although they have high negative reduction potential values. Explain.
 - The atomic radii of the elements in a transition series do not vary much while they do vary in the case of s and p-block elements. Explain.
 - The second and third members in each group of the transition elements have similar atomic radii. Explain.

These nine elements earlier made up of Group VIII in the old Mendeleev periodic table. The horizontal similarities between these elements are greater than anywhere else in the periodic table. Fe, Co and Ni are together called 'Ferrous metals' and Ru, Rh, Pd, Os, Ir, Pt are known as 'platinum metals'.

6.27.1 IRON AND ITS COMPOUNDS

Fe is a silvery metal which is not very hard and quite reactive. It is used in large quantities in steel making. Its biological importance is as an electron carrier in plants and animals, as haemoglobin in mammals, as nitrogenase to fix bacteria and many more. Fe is strongly ferromagnetic but the ferromagnetism is lost above the Curie temperature which is $700^\circ C$ for Fe.

Iron is passivated by strong oxidising agents like conc. HNO_3 , $K_2Cr_2O_7$ due to the formation of a protective coat of oxide (Fe_2O_3) while with dilute acids Fe is oxidised to Fe^{2+} . Finely divided iron combines with the ligand CO forming $[Fe(CO)_5]$ which is liquid at room temperature.

Rusting of iron is a special case of corrosion and is of great importance. Rusting occurs in the presence of O_2 , H_2O and H^+ due to the formation of an oxide film of Fe_2O_3 which is not protective and the corrosion continues. To prevent corrosion, O_2 and H_2O must be excluded. This is done by electroplating Fe with a thin layer of Sn (tin plating), dipping the Fe in molten zinc (hot dipping), electroplating with Zn (galvanising) or painting with red lead.

+2 O.S. of Fe is more stable and salts are called ferrous salts. In aqueous solutions, ferrous salts are pale green and contain the $[Fe(H_2O)_6]^{2+}$ ion.

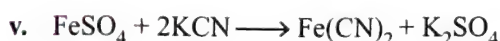
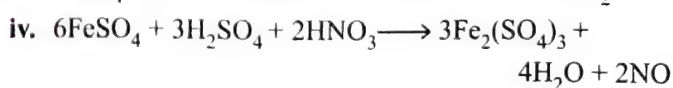
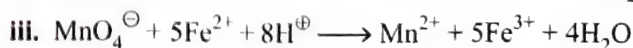
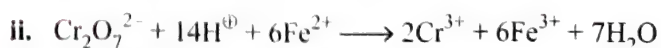
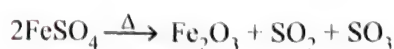
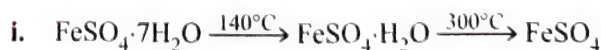
6.27.2 FERROUS SULPHATE [$FeSO_4 \cdot 7H_2O$] (GREEN VITRIOL)

Preparation:

- $FeCO_3 + H_2SO_4 \longrightarrow FeSO_4 + H_2O + CO_2$
- $FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$ (Kipp's apparatus)
- $2FeS_2 + 2H_2O + 7O_2 \longrightarrow FeSO_4 + 2H_2SO_4$
- $Fe + H_2SO_4(dil.) \longrightarrow FeSO_4 + H_2$

Properties:

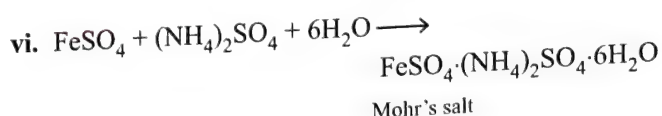
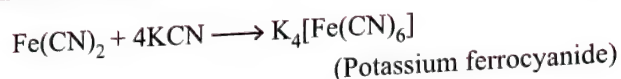
- It is a **pale green** crystalline solid, soluble in water.
- It is an efflorescent substance, and is isomorphous with Epsom salt ($MgSO_4 \cdot 7H_2O$) and white vitriol ($ZnSO_4 \cdot 7H_2O$).
- It turns brown due to oxidation into the ferric compounds by atmospheric oxygen.



6.27 COMPOUNDS AND ALLOYS OF TRANSITION METALS

Compounds of iron, cobalt and nickel groups:

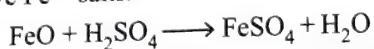
Group 8	Group 9	Group 10	
Fe	Co	Ni	Ferrous metals
Ru	Rh	Pd	Less occurring platinum metals
Os	Ir	Pt	More occurring platinum metals

**Uses:**

1. It is used in the preparation of writing ink, Mohr's salt and in the extraction of gold.
2. It is used as laboratory reagent and as a mordant in dyeing.

6.27.3 FERROUS OXIDE (FeO)

It is a black powder, basic in nature and reacts with dilute acids to give Fe^{2+} salts.



It is used in glass industry to impart green colour to glass.

6.27.4 FERROUS OXIDE (Fe_2O_3) OR JEWELLER'S ROUGE**Preparation:**

1. $2\text{FeSO}_4 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$ (Lab. Method)
2. $4\text{FeS} + 7\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 4\text{SO}_2$
3. $2\text{Fe}(\text{OH})_3 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$

Properties:

It is in the form of red powder, insoluble in water and liberates oxygen when heated at 1300°C .

1. $6\text{Fe}_2\text{O}_3 \xrightarrow{1300^\circ\text{C}} 4\text{Fe}_3\text{O}_4 + \text{O}_2$
2. $\text{Fe}_2\text{O}_3 + 2\text{NaOH} \xrightarrow{\text{Fusion}} 2\text{NaFeO}_2 + \text{H}_2\text{O}$
 $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{NaFeO}_2 + \text{CO}_2$
 (Amphoteric in nature)
3. It is reduced to Fe as:
 $\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 2\text{Fe} + 3\text{CO}$
 $\text{Fe}_2\text{O}_3 + 3\text{H}_2 \longrightarrow 2\text{Fe} + 3\text{H}_2\text{O}$
 $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$
4. $\text{Fe}_2\text{O}_3 + 6\text{HCl} \longrightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O}$

Uses:

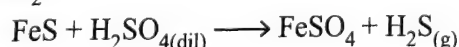
1. It is used as a red pigment.
2. It is used as a catalytic agent for oxidation of CO to CO_2 in Bosch Process.
3. A finely powdered form of Fe_2O_3 is called Jeweller's rouge. It is used for polishing jewellery.

6.27.5 FERROSOFERRIC OXIDE (Fe_3O_4)

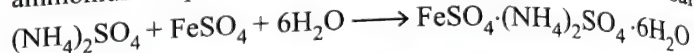
It is a mixed oxide of FeO and Fe_2O_3 . It is more stable than FeO and Fe_2O_3 , magnetic in nature and dissolves in acids giving a mixture of Fe^{2+} and Fe^{3+} salts.

**6.27.6 FERROUS SULPHIDE (FeS)**

It is prepared by heating Fe filling with S. With dilute H_2SO_4 , it gives H_2S .

**6.27.7 MOHR'S SALT ($\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$)**

It is prepared from FeSO_4 and $(\text{NH}_4)_2\text{SO}_4$ and is known as ferrous ammonium sulphate and is a light green coloured double salt.

**6.27.8 FERRIC CHLORIDE (FeCl_3)****Preparation:**

1. $2\text{Fe} + 3\text{Cl}_2 \longrightarrow 2\text{FeCl}_3$ (Anhydrous)
2. Hydrated $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ can be prepared by dissolving iron in aqua regia or iron oxide in hydrochloric acid then by crystallising the solution.
 $2\text{Fe} + 4\text{HCl} + \text{Cl}_2 \longrightarrow 2\text{FeCl}_3 + 2\text{H}_2$
 $\text{Fe}_2\text{O}_3 + 6\text{HCl} \longrightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O}$

Properties:

1. Hydrated $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is yellow deliquescent crystalline solid, soluble in water, alcohol and ether, whereas anhydrous FeCl_3 is dark solid.
2. It forms addition compounds like $\text{FeCl}_3 \cdot 6\text{NH}_3$, $\text{FeCl}_3 \cdot \text{NOCl}$ (Tilden reagent)
 - i. $\text{FeCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Fe}(\text{OH})_3 + 3\text{HCl}$
 - ii. It decomposes at 500°C .
 $2\text{FeCl}_3 \xrightarrow{\Delta} 2\text{FeCl}_2 + \text{Cl}_2$
 - iii. $4\text{FeCl}_3 + 3\text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{HCl}$
 Ferri ferro cyanide (Prussian blue)
 - iv. $2\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$ (Oxidising)
 - v. Oxidising action:
 $2\text{FeCl}_3 + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{FeCl}_2 + \text{H}_2\text{SO}_4 + 2\text{HCl}$
 $2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$

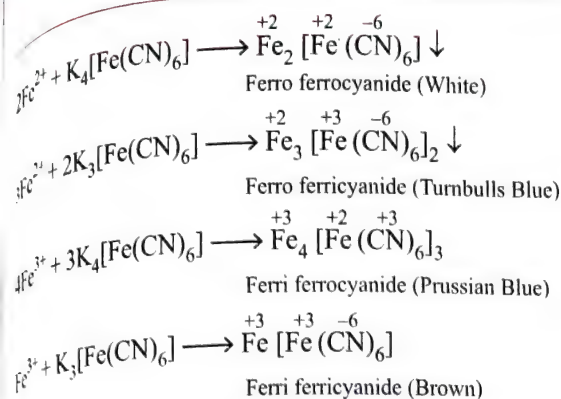
Uses:

1. It is used in medicine as disinfectant.
2. It is used in medicine to stop bleeding as it coagulates.
3. It is used in laboratory as a reagent (oxidising).

Thermal decomposition of FeC_2O_4 :

**6.28 CYANIDE COMPLEX OF IRON**

Iron forms two important complexes with the cyanide ion namely hexacyanoferrate (II) $\{[\text{Fe}^{2+}(\text{CN})_6]^{4-}\}$ and hexacyanoferrate(III) $[\text{Fe}^{3+}(\text{CN})_6]^{3-}$. Hexacyanoferrate(II) is also known as ferrocyanide ion while hexacyanoferrate(III) is also known as ferricyanide ion. Both these ions form coloured salts with metal ions like K^+ , Cu^{2+} , Fe^{2+} which are used in qualitative analysis. Potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ is a yellow coloured solid which is famously used to detect Fe^{2+} (and Fe^{3+}) ions in solution. It forms a white coloured precipitate with Fe^{2+} and a Prussian blue solution with Fe^{3+} ions. Potassium ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$ can also be used for the same purpose as it gives Turnbulls blue colour with Fe^{2+} and a brown colour with Fe^{3+} . The reactions are:



One of the best tests for Fe^{3+} is to add aqueous solutions containing SCN^- ions. A blood red colour is produced due to a mixture of $\text{Fe}(\text{SCN})_3$ and $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$.

Prussian blue:

- (i) It can also be represented as $\text{K}^+[\text{Fe}^{+3}\text{Fe}^{+2}(\text{CN})_6]$ (potassium ferric ferro hexacyanide) (I) in addition to $\text{Fe}_4^{+3}[\text{Fe}^{+2}(\text{CN})_6]_3$ (II). I and II are prepared as:
- $$\text{Fe}^{+3} + [\text{Fe}^{+2}(\text{CN})_6]^{4-} \longrightarrow [\text{Fe}^{+3}\{\text{Fe}^{+2}(\text{CN})_6\}]^{\ominus} \quad (\text{I})$$
- $$4\text{Fe}^{+3} + 3[\text{Fe}^{+2}(\text{CN})_6]^{4-} \longrightarrow \text{Fe}_4^{+3}[\text{Fe}^{+2}(\text{CN})_6]_3 \quad (\text{II})$$

Prussian blue (I) is used as a dye for blue print paper, for ink and as a bluing agent in laundry industry.

Prussian blue (II) is used as a permanent blue pigment which has great covering power.

- (ii) When FeCl_3 solution is added to $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution, in addition to $[\text{Fe}^{3+}\{\text{Fe}^{2+}(\text{CN})_6\}]^{\ominus}$, $[\text{Fe}^{+2}\{\text{Fe}^{+3}(\text{CN})_6\}]^{\ominus}$ is also formed due to side redox reaction.
- (iii) When (I) is oxidised by Cl_2 or HNO_3 , it gives a green pigment, called **Berlingreen** (ferri ferri cyanide is obtained)
- $$2\text{KFe}^{3+}[\text{Fe}^{+2}(\text{CN})_6] + \text{Cl}_2 \longrightarrow 2\text{K} + \text{Fe}^{+3}[\text{Fe}^{+3}(\text{CN})_6]$$
- Berlin green
- (iv) With alkali, it gets decomposed to form $\text{K}_4[\text{Fe}(\text{CN})_6]$ and a brown precipitate of $\text{Fe}(\text{OH})_3$
- $$\text{KFe}[\text{Fe}(\text{CN})_6] + 3\text{KOH} \longrightarrow \text{K}_4[\text{Fe}(\text{CN})_6] + \text{Fe}(\text{OH})_3$$
- Brown ppt.
- (v) $[\text{Fe}^{+3}\{\text{Fe}^{+2}(\text{CN})_6\}]^{\ominus}$ is diamagnetic.

Turnbulls Blue:

- (i) It can also be represented as $\text{K}^+[\text{Fe}^{+2}\{\text{Fe}^{+3}(\text{CN})_6\}]^{\ominus}$ (potassium ferro ferric hexacyanide) (III) in addition to $\text{Fe}_3^{+2}[\text{Fe}^{+3}(\text{CN})_6]_4$ (iv) (III) and (IV) are prepared as:
- $$\text{Fe}^{+2} + [\text{Fe}^{+3}(\text{CN})_6]^{3-} \longrightarrow [\text{Fe}^{+2}\{\text{Fe}^{+3}(\text{CN})_6\}]^{\ominus} \quad (\text{III})$$
- $$3\text{Fe}^{+2} + 4[\text{Fe}^{+3}(\text{CN})_6]^{3-} \longrightarrow \text{Fe}_3^{+2}[\text{Fe}^{+3}(\text{CN})_6]_4 \quad (\text{IV})$$

- (ii) When FeCl_2 solution is added to $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution, in addition to $[\text{Fe}^{+2}\{\text{Fe}^{+3}(\text{CN})_6\}]^{\ominus}$, $[\text{Fe}^{+3}\{\text{Fe}^{+2}(\text{CN})_6\}]^{\ominus}$

is also obtained due to side redox reaction.

- (iii) $[\text{Fe}^{+2}\{\text{Fe}^{+3}(\text{CN})_6\}]^{\ominus}$ is paramagnetic.
- (iv) Blue colour of Turnbull's blue is less intense than blue colour of prussian blue.

ILLUSTRATION 6.18

A hydrated metallic salt A, light green in colour, gives a white anhydrous residue B after being heated gradually. B is soluble in water and its aqueous solution reacts with NO to give a dark brown compound C. B on strong heating gives a brown residue D and a mixture of two gases E and F. The gaseous mixture, when passed through acidified KMnO_4 discharges the pink colour, when passed through acidified BaCl_2 solution, gives a white precipitate. Identify A, B, C, D, E and F

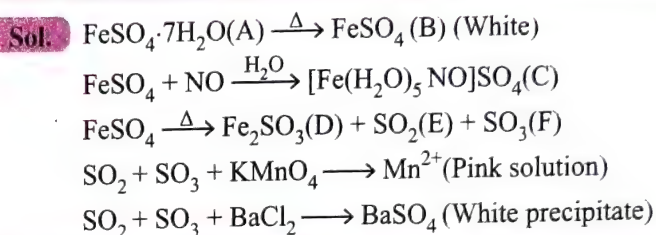


ILLUSTRATION 6.19

Which of the following statements is correct?

- Nickel is a silver white metal.
- Nickel dimethylglyoxime is square planar.
- Among complexes of cobalt the most stable are those of Co^{2+} .
- Among simple compounds of cobalt the most stable are those of Co^{2+} .

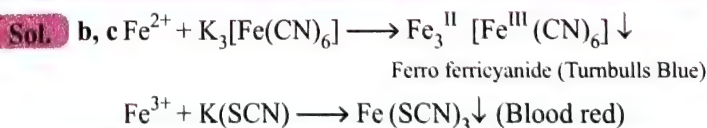
Sol. a, b, d

Co^{2+} state is stable in simple compounds of cobalt while the $+3$ state is more stable in complexes.

ILLUSTRATION 6.20

Which of the following statement(s) is(are) correct with reference to the ferrous and ferric ions?

- Fe^{3+} gives brown colour with potassium ferricyanide.
- Fe^{2+} gives blue precipitate with potassium ferricyanide.
- Fe^{2+} gives red colour with potassium thiocyanate.
- Fe^{2+} gives brown colour with ammonium thiocyanate.



6.29 COBALT AND ITS COMPOUNDS

Cobalt is a very tough metal which resembles iron. It is bluish white and lustrous in appearance. Like iron it is ferromagnetic (Curie temperature = 1000°C) but relatively unreactive as it does not react with H_2O , H_2 or N_2 . However, it forms the most number of complexes and more compounds than any other element except carbon.

6.29.1 Co²⁺ STATE

+II state is the most important oxidation state for simple compounds of cobalt. Some compounds in this state are CoO, CoCl₂, CoSO₄, CoCO₃. The hydrated salts are all pink or red due to the hexahydrate ion [Co(H₂O)₆]²⁺ while CoO is olive green. Thus CoCl₂ is used as a test for water and as an indicator added to the drying agent 'silica gel'. CoO in combination with ZnO is used as a green pigment in paints called Rinnmann's green.

6.29.2 Co³⁺ STATE

+III state is the most important state for complexes of cobalt. Since the (+II) state is common for simple compounds, it is difficult to oxidise Co²⁺ to Co³⁺ and Co³⁺ are less stable and are reduced by water. In contrast many Co(+II) complexes are readily oxidised to Co(+III) complexes, Co(+III) complexes being more stable.

6.30 NICKEL AND ITS COMPOUNDS

Nickel, a silvery white metal which does not tarnish in air is produced in large quantities and used in a wide variety of alloys both ferrous and non-ferrous. All three metals (Ni, Pd, Pt) of Group 10 are used as catalysts in many reactions. For example, 'Raney Nickel' is very finely divided nickel used in reduction processes and Pd is used for hydrogenation.

Nickel is predominantly divalent in both its simple compounds and complexes. The hydrated salts are bright green coloured due to the hydrated ion [Ni(H₂O)₆]²⁺. Complexes are commonly square planar or octahedral. The red coloured complex precipitated by Ni²⁺ and dimethylglyoxime from slightly ammoniacal solution is square planar. This reaction is used both for detection and quantitative estimation of Ni.

6.31 COPPER

6.31.1 PROPERTIES OF COPPER

1. It is a reddish coloured lustrous metal, soft, malleable and ductile and is the best conductor next to silver.
2. Molten metal adsorbs (occludes) SO₂ gas which is given off on heating.
3. Non-oxidising acids HCl and dil. H₂SO₄ do not have any effect on copper. However they dissolve copper in the presence of air.

$$2\text{Cu} + 4\text{HCl (dil.)} + \text{O}_2 \longrightarrow 2\text{CuCl}_2 + 2\text{H}_2\text{O}$$

$$6\text{Cu} + 6\text{HCl (conc.)} + 3\text{O}_2 \longrightarrow 3\text{CuCl}_2 \cdot 3\text{Cu(OH)}_2$$

Atacamite

$$2\text{Cu} + 2\text{H}_2\text{SO}_4 \text{ (dil.)} + \text{O}_2 \longrightarrow 2\text{CuSO}_4 + 2\text{H}_2\text{O}$$

$$\text{Cu} + 2\text{H}_2\text{SO}_4 \text{ (conc.)} \longrightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$$
4. Cu reacts with SO₂ in air.

$$8\text{Cu} + 6\text{H}_2\text{O} + 2\text{SO}_2 + 5\text{O}_2 \longrightarrow 2[\text{CuSO}_4 \cdot 3\text{Cu(OH)}_2]$$

Bronchantite
5. It produces green coating of basic copper carbonate [CuCO₃·Cu(OH)₂] in presence of moisture and CO₂ in air (O₂). It is also known as **Copper Patina or Verdigris**.

$$2\text{Cu} + \text{H}_2\text{O} + \text{CO}_2 + \text{O}_2 \longrightarrow \text{CuCO}_3 \cdot \text{Cu(OH)}_2$$

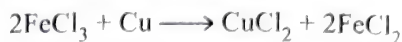
6. Dissolves in NH₄OH solution in the presence of air.

$$2\text{Cu} + 2\text{H}_2\text{O} + \text{O}_2 + 8\text{NH}_3 \longrightarrow 2[\text{Cu(NH}_3)_4(\text{OH})_2] \text{ (Blue)}$$

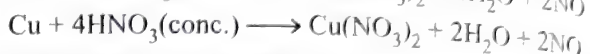
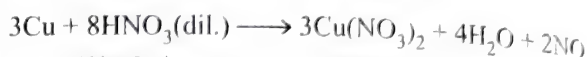
Cupra ammonium complex
7. Copper reduces oxides of nitrogen to elementary nitrogen and ferric ion to ferrous ion.



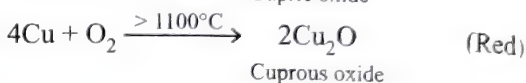
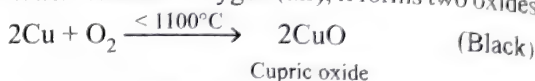
The etching of designs on copper plates using ferric chloride is based on this property.



8. Nitric acid reacts with Cu as follows:



9. When heated in oxygen (air), it forms two oxides as follows



6.31.2 USES OF COPPER

1. Copper is the second most useful metal (first being iron) because of its stability in air and water having excellent conductivity and thus is used in the manufacture of electrical wires, cables etc.
2. It is used for electroplating and electrotyping.
3. It is used for making vacuum pumps, calorimeter, steam boilers, kettles etc.
4. It is used in the manufacture of coins, copper salts and in de-silverisation of lead.

6.31.3 ALLOYS OF COPPER

Alloys	Composition	Alloy	Composition
Brass	60% Cu + 40% Zn	German silver	56% Cu + 24% Zn + 20% Ni
Gun-metal	90% Cu + 8% Sn + 2% Zn	Manganin	86–88% Cu + 13–18% Mn + 1–4% Ni
Bronze	75–90% Cu + 10–25% Sn	Bell metal	80% Cu + 20% Sn
Aluminium bronze	90% Cu + 10% Al	Constantan	60% Cu + 40% Ni
Monel metal	30% Cu + 67% Ni + 3% (Fe + Mn)		

6.32 COMPOUNDS OF COPPER

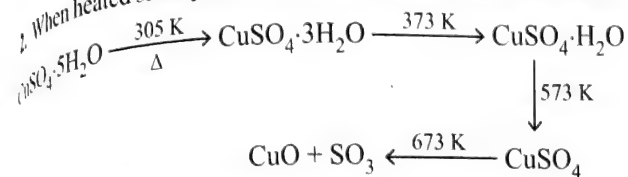
6.32.1 COPPER SULPHATE [CuSO₄·5H₂O] (BLUE VITRIOL)

Preparation:

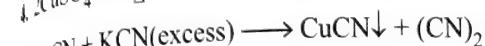
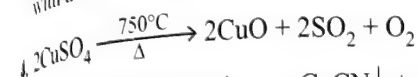
1. $\text{CuCO}_3 \cdot \text{Cu(OH)}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{CuSO}_4 + 3\text{H}_2\text{O} + \text{CO}_2$
2. $\text{CuO} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O}$
3. $\text{CuFeS}_2 + 4\text{O}_2 \longrightarrow \text{CuSO}_4 + \text{FeSO}_4$
4. $2\text{Cu} + 2\text{H}_2\text{SO}_4 + \text{O}_2 \longrightarrow 2\text{CuSO}_4 + 2\text{H}_2\text{O}$

Properties:
1. It is a deep blue coloured crystalline solid, fairly soluble in water.

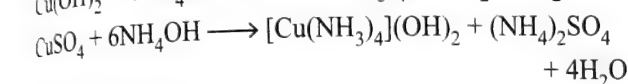
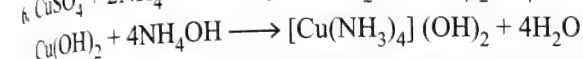
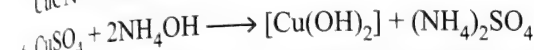
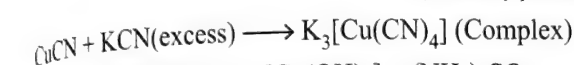
2. When heated slowly, it decomposes in the following stages:



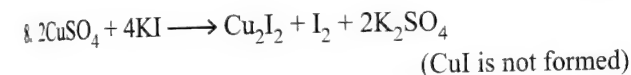
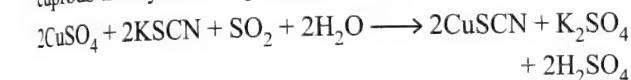
3. Anhydrous CuSO_4 regains its blue colour when moistened with a drop of water. (Test of presence of water)



Cyanogen
(extremely poisonous)



7. When dilute solution of CuSO_4 is treated with KSCN (potassium thiocyanate) and SO_2 gas is bubbled through it, cuprous thiocyanate is precipitated.



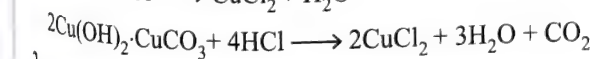
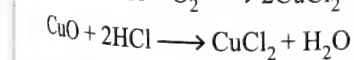
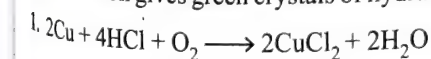
(CuI is not formed)

Uses:

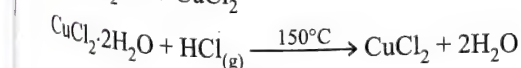
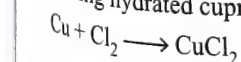
1. It is largely employed in electroplating, electric batteries.
2. It is used as a mordant for dyeing, calico printing, germ killer and fungicide.
3. It is used in medicine as antiseptic, laboratory reagent for green pigments.
4. It is used in making Fehling's solution and making Bordeaux mixture: [CuSO_4 + Lime (milk lime)] used for dusting vines, trees, potatoes to kill fungi and moulds.

6.33.2 CUPRIC CHLORIDE [$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$]

Preparation: The metal or cupric oxide or cupric hydroxide or copper carbonate is dissolved in conc. HCl. The resulting solution on crystallisation gives green crystals of hydrated cupric chloride.



2. Anhydrous cupric chloride is obtained as a dark brown mass when copper metal is heated in excess of chlorine gas or by heating hydrated cupric chloride in HCl gas at 150°C .



Properties:

1. It is a deliquescent compound and is readily soluble in water. The dilute solution is blue but concentrated solution is, however, green. It changes to yellow when conc. HCl is added. The blue colour is due to complex cation $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and yellow colour due to complex anion $[\text{CuCl}_4]^{2-}$ and green when both are present.
2. The aqueous solution is acidic due to its hydrolysis.
$$\text{CuCl}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Cu}(\text{OH})_2 + 2\text{HCl}$$
3.
$$\text{CuCl}_2 + 2\text{NaOH} \longrightarrow \text{Cu}(\text{OH})_2 + 2\text{NaCl}$$

$$\text{CuCl}_2 + 3\text{Cu}(\text{OH})_2 \longrightarrow \text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$$
4.
$$3(\text{CuCl}_2 \cdot 2\text{H}_2\text{O}) \longrightarrow \text{CuO} + \text{Cu}_2\text{Cl}_2 + 2\text{HCl} + \text{Cl}_2 + 5\text{H}_2\text{O}$$

$$2\text{CuCl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Cu}_2\text{Cl}_2 + 2\text{HCl} + \text{H}_2\text{SO}_4$$

$$2\text{CuCl}_2 + \text{SnCl}_2 \longrightarrow \text{Cu}_2\text{Cl}_2 + \text{SnCl}_4$$
5.
$$\text{CuCl}_2 + 4\text{NH}_4\text{OH} \longrightarrow \text{Cu}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O}$$

Uses:

1. It is used as an oxygen carrier in the preparation of organic dye stuffs.
2. It is used in medicines.
3. It is used as catalyst in Deacon's process for the preparation of Cl_2 .

6.32.3 CUPRIC OXIDE [(CuO) BLACK COPPER OXIDE]

Preparation:

1. By heating Cu_2O in air or by heating copper for a long time in air.
$$2\text{Cu}_2\text{O} + \text{O}_2 \xrightarrow{\Delta} 4\text{CuO}$$

$$2\text{Cu} + \text{O}_2 \xrightarrow{\Delta} 2\text{CuO}$$
2. By heating copper nitrate.
$$2\text{Cu}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$$
3. By heating cupric hydroxide and basic copper carbonate.
$$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$$

$$\text{Cu}(\text{OH})_2 \xrightarrow{\Delta} \text{CuO} + \text{H}_2\text{O}$$

$$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \xrightarrow{\Delta} 2\text{CuO} + \text{H}_2\text{O} + \text{CO}_2$$

Properties:

1. It is a black powder, stable to moderate heating.
2.
$$\text{CuO} + 2\text{HCl} \longrightarrow \text{CuCl}_2 + \text{H}_2\text{O}$$

$$\text{CuO} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O}$$

$$\text{CoO} + 2\text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{O}$$
3.
$$\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O}$$

$$\text{CuO} + \text{C} \longrightarrow \text{Cu} + \text{CO}$$

$$\text{CuO} + \text{CO} \longrightarrow \text{Cu} + \text{CO}_2$$
4.
$$4\text{CuO} \xrightarrow{1100-1200^\circ\text{C}} 2\text{Cu}_2\text{O} + \text{O}_2$$

Uses:

1. It is used to impart green and blue colour to glazes and glasses.
2. It is used in petroleum to remove sulphur.

6.32.4 Cuprous Oxide [(Cu₂O) Red Copper Oxide]

In nature it occurs as cuprite known as red copper ore.

Preparation: It may be prepared by any one of the following methods:

1. $\text{CuO} + \text{Cu} \xrightarrow{\text{Heat}} \text{Cu}_2\text{O}$
2. Reduction of CuO or compounds or mixture containing CuSO₄.

$$2\text{CuO} + \text{Glucose} \longrightarrow 2\text{Cu}_2\text{O} + \text{Gluconic acid}$$

or Aldehyde or HCOOH Red ppt

$$2\text{CuSO}_4 + 2\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_3 \longrightarrow \text{Cu}_2\text{O} + 3\text{Na}_2\text{SO}_4 + 2\text{CO}_2$$

Properties:

1. Red powder, insoluble in water and alkalis.
2. It can be oxidised to CuO by heating it in air.

$$2\text{Cu}_2\text{O} + \text{O}_2 \xrightarrow{\Delta} 4\text{CuO}$$
3. It can be reduced to copper when heated with carbon or in a current of H₂ or CO.

$$\text{Cu}_2\text{O} + \text{C} \longrightarrow 2\text{Cu} + \text{CO}$$

$$\text{Cu}_2\text{O} + \text{H}_2 \longrightarrow 2\text{Cu} + \text{H}_2\text{O}$$

$$\text{Cu}_2\text{O} + \text{CO} \longrightarrow 2\text{Cu} + \text{CO}_2$$
4. Similarly hot nitric acid is reduced by Cu₂O.

$$3\text{Cu}_2\text{O} + 14\text{HNO}_3(\text{dil.}) \longrightarrow 6\text{Cu}(\text{NO}_3)_2 + 7\text{H}_2\text{O} + 2\text{NO}$$

$$\text{Cu}_2\text{O} + 2\text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{O} + \text{Cu}$$
5. Hot concentrated H₂SO₄ is reduced by cuprous oxide.

$$\text{Cu}_2\text{O} + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{CuSO}_4 + 3\text{H}_2\text{O} + \text{SO}_2$$
6. Acids dissolve and decompose Cu₂O to give cupric salt and copper.

$$\text{Cu}_2\text{O} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{Cu} + \text{H}_2\text{O}$$
7. Alkali cyanides dissolve it to yield the colourless cuprocyanide complex.

$$\text{Cu}_2\text{O} + 6\text{KCN} + \text{H}_2\text{O} \longrightarrow 2\text{K}_2[\text{Cu}(\text{CN})_3] + 2\text{KOH}$$
8. Concentrated NH₄OH dissolves it to form the complex diamminecuprous hydroxide in the absence of air. In the presence of air, however, there is oxidation and diamminecupric hydroxide is formed.

$$\text{Cu}_2\text{O} + 4\text{NH}_3\text{OH} \longrightarrow 2[\text{Cu}(\text{NH}_3)_2]\text{OH} + 3\text{H}_2\text{O}$$
9. With concentrated HCl, a complex compound is formed.

$$\text{Cu}_2\text{O} + 6\text{HCl} \longrightarrow 2\text{H}_2[\text{CuCl}_3] + \text{H}_2\text{O}$$

Uses:

1. It is used in making ruby glass and enamel.
2. It is used in the manufacture of antirust paint.
3. It is used in electrical circuits as a rectifier.

ILLUSTRATION 6.21

Hydrazine reduces Fehling's solution to form:

- a. Cu(OH)₂ b. Cu₂O c. CuO d. Cu + O₂

Sol. b. Fehling's test reduces CuO to red coloured Cu₂O.

ILLUSTRATION 6.22

In the following reaction, Y and Z are respectively:



- a. AgCl, O₂ b. NO₂, N₂O₄ c. N₂O₅, O₂ d. None

Sol. c. $4\text{AgNO}_3 + 2\text{Cl}_2 \longrightarrow 4\text{AgCl}(\text{X}) + \text{N}_2\text{O}_5(\text{Y}) + \text{O}_2(\text{Z})$

ILLUSTRATION 6.23

Explain the following facts:

- a. Copper hydroxide is soluble in ammonium hydroxide but not in sodium hydroxide.
- b. Addition of an alkali to cuprous chloride solution gives a yellow precipitate which gradually changes to a red colour.

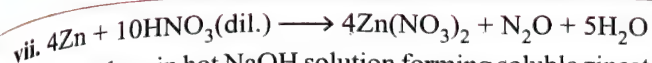
Sol.

- a. This is because Cu²⁺ can form many complexes with NH₄⁺ which are soluble in water.
- b. $\text{Cu}_2\text{Cl}_2 + 2\text{NaOH} \longrightarrow \text{Cu}_2\text{O} \downarrow + 2\text{NaCl} + \text{H}_2\text{O}$
The precipitate changes colour from yellow to red due to formation of Cu₂O.

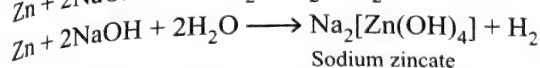
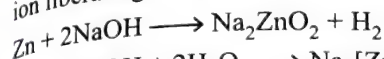
6.33 ZINC

6.33.1 PROPERTIES OF ZINC

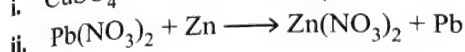
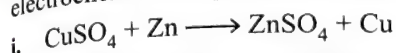
1. It is a bluish white crystalline metal brittle at ordinary temperature.
2. It is malleable and ductile at 100–150°C and again becomes brittle at 220°C.
3. When molten zinc is poured in cold water, granulated zinc is obtained.
4. $2\text{Zn} + \text{O}_2 \xrightarrow{\Delta} 2\text{ZnO}$
5. $\text{Zn} + \text{H}_2\text{O}_{(\text{g})} \longrightarrow \text{ZnO} + \text{H}_2$
Red hot
6. $4\text{Zn} + 3\text{H}_2\text{O} + \text{CO}_2 + 2\text{O}_2 \longrightarrow \text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$
7. $\text{Zn} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2$
8. It reacts with oxidising acids as follows.
 - i. $\text{Zn} + 2\text{H}_2\text{SO}_4(\text{conc.}) \longrightarrow \text{ZnSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2$
 - ii. $3\text{Zn} + 4\text{H}_2\text{SO}_4(\text{dil.}) \longrightarrow 3\text{ZnSO}_4 + \text{S} + 4\text{H}_2\text{O}$
 - iii. $4\text{Zn} + 5\text{H}_2\text{SO}_4(\text{moderately conc.}) \longrightarrow 4\text{ZnSO}_4 + \text{H}_2\text{S} + 4\text{H}_2\text{O}$
 - iv. $4\text{Zn} + 10\text{HNO}_3(\text{very dil.}) \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$
 - v. $3\text{Zn} + 8\text{HNO}_3(\text{moderately conc.}) \longrightarrow 3\text{Zn}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
 - vi. $\text{Zn} + 4\text{HNO}_3(\text{hot conc.}) \longrightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$



9. Zinc dissolves in hot NaOH solution forming soluble zincate ion liberating hydrogen.



10. Zinc, being highly electropositive metal shows lots of electrochemical displacement reactions.



6.33.2 USES OF ZINC

1. Zinc sheets are used for roofing.

2. Zn-dust is used as reducing agent and also in precipitation of silver and gold from their complex cyanides.

3. It is used in desilverisation of lead in **Parke's process**.

4. In the manufacture of Zn-Cu couple by depositing copper on zinc (dust) which reacts with water or alcohol and produces nascent hydrogen which acts as reducing agent.

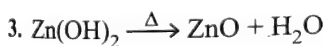
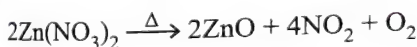
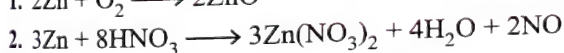
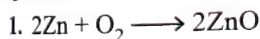
5. It is used in the making of alloys like **brass**, **german silver** and making batteries.

6. It is used for galvanising iron (deposition of thin and coherent layer of Zn on iron sheets to avoid corrosion). It is achieved by dipping iron plates in molten zinc.

6.34 COMPOUNDS OF ZINC

6.34.1 ZINC OXIDE [ZnO]

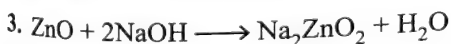
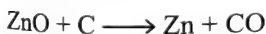
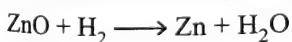
Preparation:



Properties:

1. It is white, light powder insoluble in water and known as **Philosopher's Wool**. On heating it becomes yellow and on cooling it becomes white.

2. It is reduced to Zn by the reaction of charcoal or dry H_2 .



Uses:

1. It is used as white paint and in the manufacture of glass and pottery glazes.

2. It is used in medicine as zinc ointment.

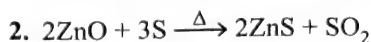
3. It is used in xerox printing, white shoe polish, a filler for rubber.

4. It does not tarnish even in H_2S as ZnS is also white in colour.

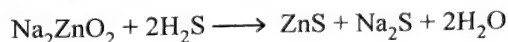
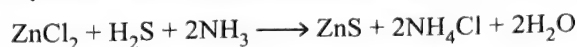
5. Mixture of ZnO and ZnCl_2 forms good cement for teeth.

6.34.2 ZINC SULPHIDE [ZnS]

Preparation:



3. By the reaction of ammonical solution of zinc salt and H_2S .



Properties:

1. It turns yellow on exposure to light.

2. It is a white solid insoluble in water and acetic acid and soluble in mineral acids.

3. Due to impurities of sulphides of Mn, Cu, Ag, etc. it shows phosphorescence.

Uses:

1. It is used in luminous paint on watch dials (one part Ra in 10 million ZnS).

2. It is used as a phosphorescent.

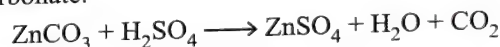
3. It is used for X-ray screen in radioactive work.

4. It is used in white paint: **Lithopone** ($\text{ZnS} + \text{BaSO}_4$).

6.34.3 Zinc Sulphate [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$] (White Vitriol)

Preparation:

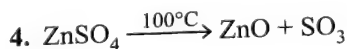
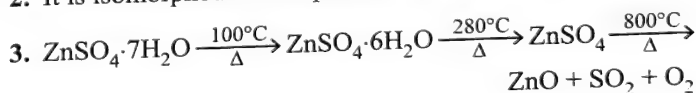
It is prepared by the action of dil. H_2SO_4 on Zn metal or its oxide or carbonate.



Properties:

1. It is highly soluble in water.

2. It is isomorphous with epsom salt and green vitriol.



Uses:

1. It is used in medicine as an eye lotion.

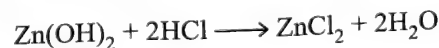
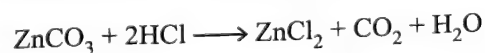
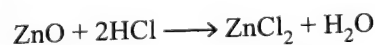
2. It is used in dyeing industry.

3. It is used in the manufacture of Lithopone.

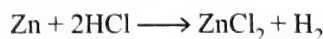
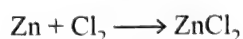
6.34.4 ZINC CHLORIDE [ZnCl_2]

Preparation:

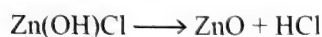
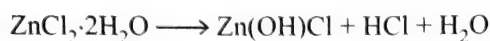
1. It is obtained by treating zinc oxide or zinc carbonate or zinc hydroxide with dilute HCl. The solution on concentration and cooling gives hydrated ZnCl_2 crystals, $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$.



2. Anhydrous zinc chloride is obtained by heating zinc in the atmosphere of dry chloride or dry HCl gas.

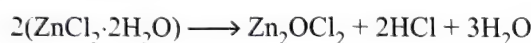
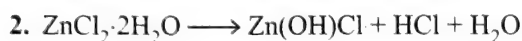


3. Anhydrous ZnCl_2 cannot be obtained by heating zinc chloride as on hydrolysis, basic chloride (zinc hydroxy chloride) is formed which on further heating gives zinc oxide.

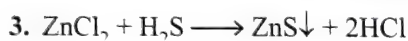


Properties:

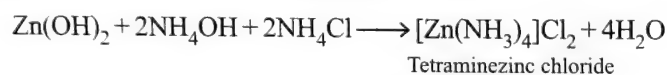
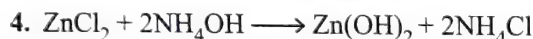
1. Anhydrous ZnCl_2 is white solid, deliquescent and soluble in water. It melts at 660°C and boils at 730°C .



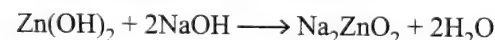
Zinc oxychloride



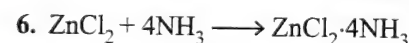
White precipitate



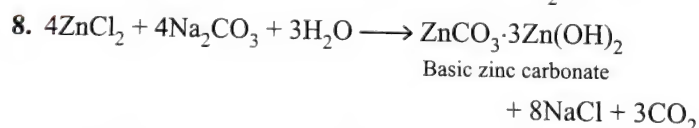
Tetraminezinc chloride



Sodium zincate



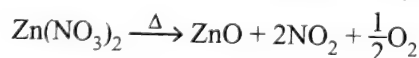
7. Its syrupy solution when mixed with zinc oxide. ZnO sets to a hard mass forming an oxychloride, $\text{ZnCl}_2 \cdot 3\text{ZnO}$.



Basic zinc carbonate



9. Thermal decomposition of $\text{Zn}(\text{NO}_3)_2$.



Uses:

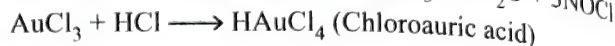
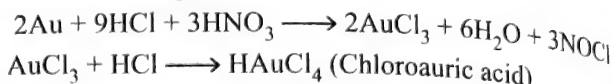
1. It is used as dehydrating agent.
2. The concentrated solution of ZnCl_2 is used for impregnating timber to prevent its destruction by the action of micro-organisms.
3. The mixture of syrupy zinc chloride solution and zinc oxide is used for dental filling.

6.35 GOLD

6.35.1 PROPERTIES OF GOLD

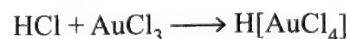
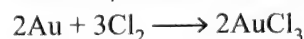
1. Gold is a soft, heavy and yellow metal with high lustre.
2. It is a good conductor of heat and electricity and has a high melting and boiling points.
3. It is highly malleable and ductile.

4. It is not attacked by ordinary air (oxygen), water or steam. It does not displace hydrogen from acids. It is not attacked even by strong alkalies. It however dissolves in aqua regia (3 parts of conc. HCl and 1 part conc. HNO_3) to give auric chloride, AuCl_3 .

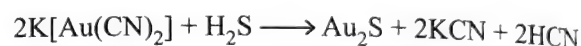


6.35.2 COMPOUNDS OF GOLD

1. **AuCl_3 :** Gold reacts with chlorine to form chloride. It is a reddish solid soluble in H_2O . It reacts with HCl to give $\text{H}[\text{AuCl}_4]$ which is used in toning process in photography.



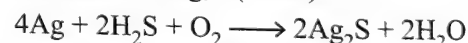
2. **Au_2S :** It is a dark brown solid insoluble in water and is prepared as follows:



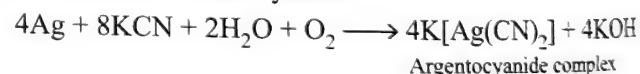
6.36 SILVER

6.36.1 PROPERTIES OF SILVER

1. It is a lustrous white metal, which is ductile and malleable and a very good conductor of heat and electricity (better than copper).
2. On heating the molten mass of silver absorbs oxygen which is again released on cooling. This is called as **spitting of silver**.
3. There is no effect of air and alkalies on silver.
4. The air contaminated with H_2S tarnishes silver due to formation of Ag_2S (black).



5. It dissolves in alkali cyanide.



Argentocyanide complex

6. $3\text{Ag} + 4\text{HNO}_3(\text{dil.}) \longrightarrow 3\text{AgNO}_3 + 2\text{H}_2\text{O} + \text{NO}$



7. Dil. H_2SO_4 has no action on silver.



6.36.2 USES OF SILVER

1. It is used in preparation of silver slates. It is used for photography and as conductor of electricity (the best conductor of electricity).
2. It is used in silver plating.
3. Silver leaves are used in **Ayurvedic** and **Yunani** medicines.
4. Alloyed with Cu, it is used in making coins, jewellery and decorative articles and silver wares.
5. Silver amalgam is used for filling teeth.

6.37 COMPOUNDS OF SILVER

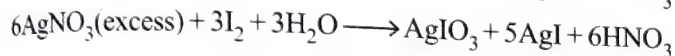
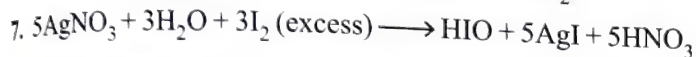
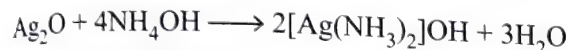
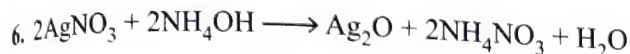
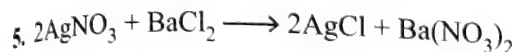
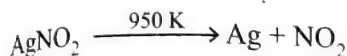
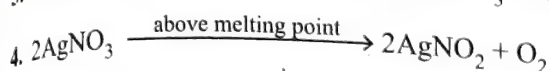
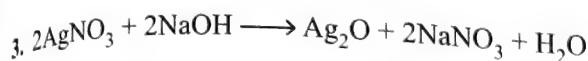
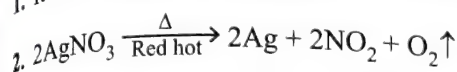
6.37.1 SILVER NITRATE $[\text{AgNO}_3]$ (LUNAR CAUSTIC)

Preparation:

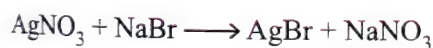


Properties:

1. It is a colourless crystalline solid, soluble in water.

**Uses:**

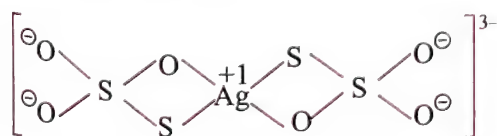
1. It is used in photography.
2. It is used in making of marking ink used for marking linen.
3. It is used in silvering mirrors.
4. It has a caustic and destructive effect of organic tissues. It produces burning sensation (like caustic) and reduces to metallic silver which is white like the lunar moon, hence the name **lunar caustic**.
5. In small doses it is used as a medicine in nervous diseases.

6.37.2 SILVER BROMIDE [AgBr]**Preparation:****Properties:**

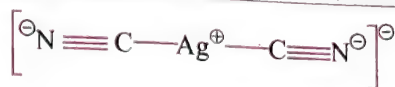
1. It is a pale yellow white solid, insoluble in water and conc. HNO_3 but soluble in excess of NH_4OH .
2. $\text{AgBr} + 2\text{KCN} \longrightarrow \text{K}[\text{Ag}(\text{CN})_2] + \text{KBr}$
3. $\text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + \text{NaBr}$
4. $\text{AgBr} + 2\text{NH}_4\text{OH} \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Br} + 2\text{H}_2\text{O}$

Note:

- i. AgCl , AgBr , AgI are insoluble in H_2O . It is due to high lattice energy of these compounds.
 - ii. AgF is soluble in H_2O . It is due to large (negative hydration enthalpy of F^- ions.).
5. All the silver halides (AgX) dissolve in thiosulphate ($\text{S}_2\text{O}_3^{2-}$) and cyanide (CN^-) solution giving thiosulphato and dicyano complexes of Ag^+ ion, as shown in Figures and respectively.



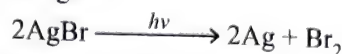
Structure of dithiosulphato argentate(I) ion



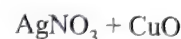
Structure of dicyanoargentate(I) ion

Uses:

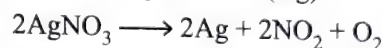
1. AgBr is used in photographic films, since it is very sensitive to light.



2. Recovery of Ag and Cu from its alloy:



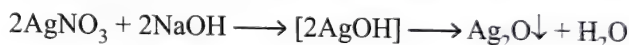
AgNO_3 and CuO are washed in water. CuO is obtained as residue and the filtrate contains AgNO_3 . The filtrate is heated strongly to give silver (Ag).



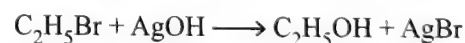
The residue is dissolved in dil. H_2SO_4 to obtain CuSO_4 . CuSO_4 is treated with iron scrap to get Cu .

**6.37.3 SILVER OXIDE [Ag₂O]**

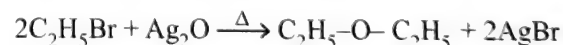
Preparation: It is prepared as brown solid by adding sodium hydroxide solution to silver nitrate solution.

**Properties:**

1. It is brown solid and sparingly soluble in water.
2. On heating, it is decomposed to black metallic silver with evolution of oxygen at 160°C
3. The aqueous solution is strongly basic, solution behaving as AgOH . Moist silver oxide hydrolyses the alkyl halide to alcohol.



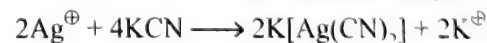
4. Dry distillation of a mixture of alkyl halide with silver oxide produces ether.



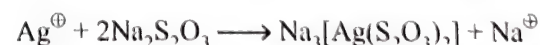
5. It forms colourless soluble complexes with ammonia. KCN and sodium thiosulphate.



Diammine silver(I) hydroxide (Tollens reagent)

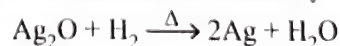


Potassium dicyanoargentate(I)



Sodium bis-thiosulphatoargentate(I)

6. It is reduced to the metal by hydrogen on heating

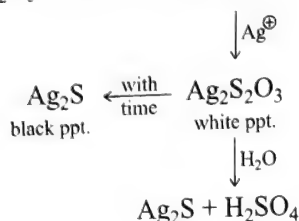
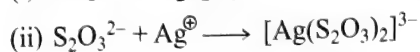
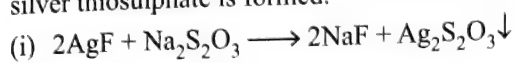
**Uses:**

1. It is used as Tollen's reagent for the detection of aldehydes, formic acid and terminal alkynes.
2. It is used in the manufacture of mirrors.

6.37.4 SILVER THIOSULPHATE [$\text{Ag}_2\text{S}_2\text{O}_3$]

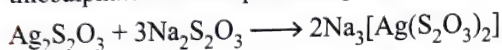
Preparation:

- When sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$ is added to a solution of silver acetate or nitrate or fluoride, a white precipitate of silver thiosulphate is formed.

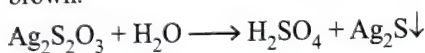


Properties:

- It forms needle like crystals. It dissolves in excess of sodium thiosulphate solution producing a complex.



- Silver thiosulphate is decomposed by water giving a variety of colours, changing from white to black through yellow and brown.

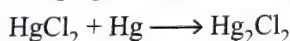


6.38 COMPOUNDS OF MERCURY

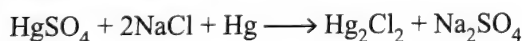
6.38.1 MERCUROS CHLORIDE [Hg_2Cl_2] (CALOMEL)

Preparation:

- It is prepared by subliming mercury and mercuric chloride.



- It is also prepared by mixture of mercuric sulphate, common salt and mercury.



Properties:

- It is known as calomel and used in calomel electrode which is widely employed in connection with electrochemical measurements.
- It is an ionic compound and ionises in solution to give 3 ions as shown:

$$\text{Hg}_2\text{Cl}_2 \longrightarrow \underbrace{\text{Hg}_2^{2+} + 2\text{Cl}^{\ominus}}_{3 \text{ ions}}$$
- It is called corrosive sublimate because it is highly poisonous (corrosive) and undergoes sublimation.
- It is a white powder which turns black with NH_3 . The reaction is used in detection of mercurous ions.

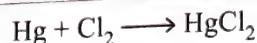
$$\text{Hg}_2\text{Cl}_2 + 2\text{NH}_3 \longrightarrow (\text{Hg} + \text{HgNH}_2\text{Cl}) + \text{NH}_4\text{Cl}$$

Brownish-black
- It is non-poisonous.

6.38.2 MERCURIC CHLORIDE [HgCl_2] (CORROSIVE SUBLIMATE)

Preparation:

- Mercuric chloride is formed by the action of chlorine on Hg.



- It is also formed by a mixture of mercuric sulphate and common salt.



Properties:

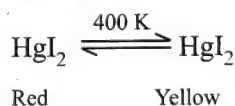
- It is a colourless crystalline solid, soluble in hot water.
- It is a covalent compound and does not ionise in the solution. It is a poisonous compound and its antidote is white of an egg.
- Its characteristic reactions are with SnCl_2 , NH_3 and KI.
 - $2\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$
 $\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \longrightarrow 2\text{Hg} + \text{SnCl}_4$
 - $\text{HgCl}_2 + 2\text{NH}_3 \longrightarrow \text{HgNH}_2\text{Cl} + \text{NH}_4\text{Cl}$
 - $\text{HgCl}_2 + 2\text{KI} \longrightarrow \text{HgI}_2 + 2\text{KCl}$
 $\text{HgI}_2 + 2\text{KI} \longrightarrow \text{K}_2\text{HgI}_4$
 (A solution of this complex in alkali is called Nessler's reagent.)
- Its very dilute solution (0.1%) is used as an antiseptic.

6.38.3 MERCURIC IODIDE [HgI_2]

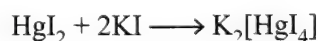
- It is prepared by reacting HgCl_2 with KI.



- It is a yellow solid below 400 K but changes to red solid above 400 K.



- It dissolves in excess of KI forming K_2HgI_4 .



- Alkaline solution of $\text{K}_2[\text{HgI}_4]$ is called Nessler's reagent.

Thermal decomposition of $\text{Hg}(\text{NO}_3)_2$:

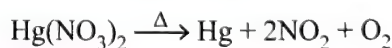


ILLUSTRATION 6.24

Write balanced equations for the reaction of alkaline perbromate with zinc giving tetrahydroxozincate anion.

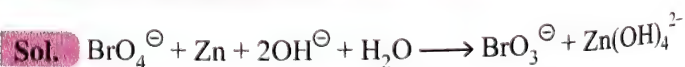


ILLUSTRATION 6.25

Excess of dilute sodium hydroxide solution is gradually added with shaking to an aqueous solution of zinc sulphate. What would you observe?

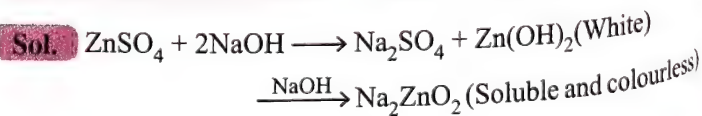


ILLUSTRATION 6.26

Explain the following:

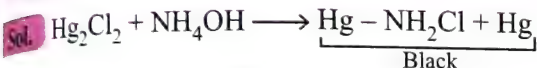
- The addition of NaOH solution to a solution of zinc chloride produces a white precipitate which dissolves on further addition of NaOH.
- The addition of NH_4OH to ZnSO_4 solution produces white precipitate but no precipitate is formed if it contains NH_4Cl .

Sol.

- First a white precipitate of $\text{Zn}(\text{OH})_2$ is formed which on further addition of NaOH forms soluble zincate Na_2ZnO_2 .
- NH_4OH is a weak hydroxide. It is ionised slightly furnishing OH^- ions which are sufficient to precipitate $\text{Zn}(\text{OH})_2$ because its low solubility product. However, in presence of NH_4Cl , the ionisation of NH_4OH is further suppressed and sufficient OH^- are not available to cause precipitation.

ILLUSTRATION 6.27

Mercurous chloride turns black on adding NH_4OH to it. Explain.

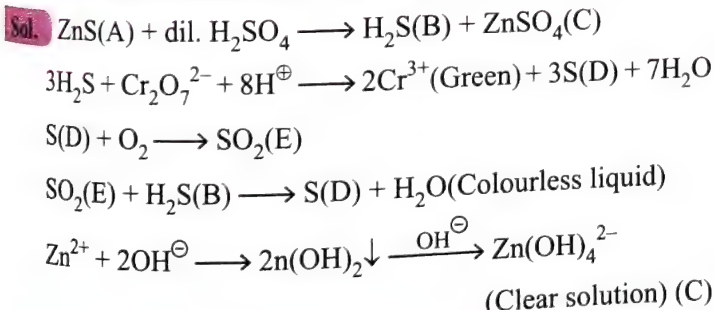


This is used to detect mercurous ions.

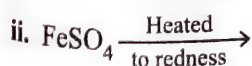
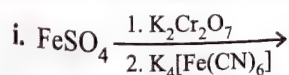
ILLUSTRATION 6.28

Identify A, B, C, D and E.

A white substance A reacts with dilute H_2SO_4 to produce a colourless gas B and a colourless solution C. The reaction between B and acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution produces a green solution and a slightly coloured precipitate D. The substance D burns in air to produce a gas E which reacts with B to yield D and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH_3 or NaOH to C produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case.

**CONCEPT APPLICATION EXERCISE 6.2****Compounds of Fe:**

- Complete and balance the following equations:



- Explain the following:

- FeCl_3 and FeBr_3 are well known, but FeI_3 has doubtful existence.
- Anhydrous FeCl_3 cannot be obtained by heating hydrated ferric chloride.
- Cast iron is hard but pure iron is soft in nature.
- A ferrous salt decolourises KMnO_4 solution.
- A ferrous salt turns brown in air.

- Draw shape of FeCl_3 in:

- Water
- Ether
- Gaseous state

- What happen when iron is treated with:

- Steam
- Dilute HNO_3

- Colourless salt A decolourises I_2 solution and gives white precipitate with AgNO_3 solution. A also changes FeCl_3 (yellow solution of FeCl_2 (Green). Identify A and explain the reactions.

- Iron forms iron(II) chloride, FeCl_2 and iron(III) chloride FeCl_3 . One of these chlorides is a dark brown solid melting 306°C . The other is a white crystalline solid with greenish tint, melts at 674°C . Which description best fits iron(II) chloride. Explain.

- Account for the following observations and write balanced chemical equations for them.

- When ferrous sulphate crystals are exposed to air, it turns brown.
- A solution of ferric chloride in water gives a brown precipitate on standing.

Compounds of Cu:

- When copper is exposed to atmosphere for a longer time, a green mass deposits on its surface. Discuss the chemical reaction involved.

- Complete and balance the following equations:



- Explain the following:

- Copper hydroxide is soluble in ammonium hydroxide but not in sodium hydroxide.
- A dark blue precipitate is formed when sodium hydroxide solution is added to copper sulphate solution. The precipitate darkens on heating.

Compounds of Zn:

- ZnO is used as a white paint inspite of the fact that it has less covering power than white lead.
 - Hydrated ZnCl_2 cannot be dehydrated on heating?
 - Zn is used in galvanisation of Fe.

Compounds of Ag:

- Preparation of looking mirrors involves the use of ammonical AgNO_3 , red lead and HCHO . Explain the function of each.

- Give reasons for the following:

- Silver ornament gets tarnished when exposed to atmosphere for a long time.

- ii. Silver nitrate solution is kept in dark coloured bottles.
 iii. Why does AgNO_3 produce a black stain on the skin.

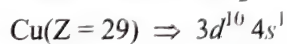
Compounds of Hg:

14. An aqueous solution containing one mole of HgI_2 and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl . Explain with equations.
15. HgCl_2 and SnCl_2 cannot coexist together in an aqueous solution.
16. Complete and balance the following equations:
- $\text{Cu(OH)}_2 + \text{NH}_4\text{NO}_3 + \text{NH}_4\text{OH} \longrightarrow \dots + \text{H}_2\text{O}$
 - $\text{Au} + \text{HCl} + \text{HNO}_3 \longrightarrow \dots + \dots + \text{H}_2\text{O}$
 - $\text{Ag}_2\text{S} + 2\text{CuCl}_2 + 2\text{Hg} \longrightarrow \dots + \dots \text{S} + 2\text{Ag}$
 - $\text{FeCl}_3 + \text{KI} \longrightarrow \dots$
 - $\text{Fe}^{2+} + \text{NO}_3^- + \text{H}^+ \longrightarrow \text{Fe}^{3+} + \dots \text{H}_2\text{O}$
 - $\text{MnO}_4^- + \text{Fe}^{2+} \longrightarrow \text{Mn}^{2+} + \text{Fe}^{3+} + \text{H}_2\text{O}$
 - $\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow$
 - $\text{HgCl}_2 + \text{SO}_2 + \dots \longrightarrow \dots$
 - $\text{CdSO}_4 + \text{NH}_4\text{OH} \longrightarrow \dots$
 - $\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow \dots$
 - $\text{Ag} + \text{CN}^- + \text{O}_2 + \dots \longrightarrow \dots \text{OH}^- + \dots$
 - $\text{CuSO}_4 + \text{KCN} \longrightarrow \dots$
 - $\text{CuSO}_4 + \text{KI} \longrightarrow \dots$
 - $\text{CuSO}_4 + \text{NH}_4\text{OH} \longrightarrow \dots + \dots$

Solved Examples**EXAMPLE 6.1**

Explain why mercury (I) ion exists as Hg_2^{2+} ion while copper (I) ion exists as Cu^+ ion.

Sol. $\text{Hg}(Z = 80) \Rightarrow 4f^{14} 5d^{10} 6s^2$; $\text{Hg}^+ \Rightarrow 4f^{14} 5d^{10} 6s^1$
 Hg^+ has one electron in its valence $6s$ -orbital, due to this Hg^+ compounds should be **paramagnetic** but actually they are **diamagnetic**. Hence the singly filled $6s$ -orbitals of the two Hg^+ ions overlap to form a Hg-Hg covalent bond. Thus, Hg^+ ions exist as dimeric species, i.e. Hg_2^{2+} .



Therefore, Cu^+ ion has no unpaired electrons to form dimeric species, i.e. Cu_2^{2+} and hence it always exists as Cu^+ ion.

EXAMPLE 6.2

Give reasons for the following:

Variations in the radii of transition elements are not as pronounced as those of representative elements.

Sol. As we proceed along a transition series, the nuclear charge increases which tends to decrease the size but the addition of electrons in the d -subshell increases the screening effect which tends to counterbalance the effect of the increased nuclear charge.

EXAMPLE 6.3

Why in any transition series, melting points first increase and then decrease and also they show a dip in the middle?

Sol. Melting points first increase because the number of unpaired electrons increases and hence strength of metallic bond increases. After reaching the maximum, the melting points decrease because the pairing of electron starts in the d -subshell and number of unpaired electrons decreases and so the strength of metallic bond decreases. The dip in the middle is due to exactly half-filled configuration of d -subshell which has higher stability. Hence electrons are held tightly by the nucleus. As a result, metallic bond is weaker.

EXAMPLE 6.4

Atomic radius of Cu is greater than that of Cr but ionic radius of Cr^{2+} is greater than that of Cu^{2+} . Give suitable explanation.

Sol. In Cu , all the d -electrons are paired ($3d^{10} 4s^1$). In Cr , all the d -electrons are unpaired ($3d^5 4s^1$). Hence, $d-d$ electron repulsions in Cu are much greater than those in Cr . Hence, Cu atom is larger in size than Cr . In Cu^{2+} ($3d^9$), $d-d$ electron repulsions decrease due to presence of one unpaired d -electron. Moreover, the electrons are attracted by 29 protons of the nucleus whereas in Cr^{2+} , three unpaired electrons are still present but they are attracted by only 24 protons of the nucleus. Thus, Cu^{2+} is smaller in size than Cr^{2+} .

EXAMPLE 6.5

Why hydrated copper sulphate is blue while anhydrous copper sulphate is white?

Sol. In $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ four water molecules are present as ligands. In the presence of these ligands d -orbitals are no longer degenerate in energy. Hence $d-d$ transition takes place absorbing red wavelength. The complementary colour, viz., blue is reflected. In anhydrous CuSO_4 , d -orbitals remain degenerate. Hence, no $d-d$ transition can occur. The white light is completely reflected back. Hence, it looks white.

EXAMPLE 6.6

Why are the ionisation energies of $5d$ elements greater than $3d$ elements?

Sol. In the $5d$ series, after lanthanum ($Z = 57$), there is lanthanoid contraction. In each group, the size of $5d$ element is smaller while nuclear charge is greater than $3d$ element. Hence, ionisation energies of $5d$ elements are greater than $3d$ elements.

EXAMPLE 6.7

Explain why cuprous chloride (CuCl) is colourless while cupric chloride (CuCl_2) is blue? or TiCl_3 is coloured while TiCl_4 is colourless?

Sol. In CuCl , Cu^{\oplus} has fully-filled d -subshell. Hence, it cannot absorb energy for $d-d$ transition. Therefore, it is colourless. In CuCl_2 , Cu^{2+} has $3d^9$ configuration, i.e., one unpaired electron is present which can absorb energy for $d-d$ transition. Hence, it is coloured. Similarly, Ti^{3+} has $3d^1$ and Ti^{4+} has empty $3d$ subshell. Hence, TiCl_3 is coloured while TiCl_4 is colourless.

EXAMPLE 6.8

The sums of first and second ionisation energies and those of third and fourth ionisation energies of nickel and platinum are:

	$\text{IE}_1 + \text{IE}_2 \text{ (MJ mol}^{-1}\text{)}$	$\text{IE}_3 + \text{IE}_4 \text{ (MJ mol}^{-1}\text{)}$
Ni	2.49	8.80
Pt	2.66	6.70

Based on this information, write

- The most common oxidation states of Ni and Pt and why.
- Name of the metal (Ni or Pt) which can more easily form compounds in its +4 oxidation state and why.

Sol.

i. The sum of the 3rd and 4th ionisation energies of nickel is much higher than the sum of 1st and 2nd ionisation energies. Hence, Ni (II) is more common. In case of platinum, the difference between $\text{IE}_3 + \text{IE}_4$ and $\text{IE}_1 + \text{IE}_2$ is much less. Hence, Pt (IV) is more common.

ii. For Ni, $\text{IE}_1 + \text{IE}_2 + \text{IE}_3 + \text{IE}_4$
 $= 2.49 + 8.80 = 11.29 \text{ kJ mol}^{-1}$
 For Pt, $\text{IE}_1 + \text{IE}_2 + \text{IE}_3 + \text{IE}_4$
 $= 2.66 + 6.70 = 9.36 \text{ kJ mol}^{-1}$.

Thus, the formation of Pt^{4+} is easier than Ni^{4+} . In other words, Pt can form compounds in the +4 oxidation state more easily.

EXAMPLE 6.9

Describe giving reason which one of the following pairs has the property indicated?

- Fe or Cu has higher melting point.
- Co^{2+} or Ni^{2+} has lower magnetic moment.

Sol.

a. Fe has higher melting point than Cu. This is because Fe has four unpaired electrons in $3d$ -subshell while Cu has only one electron in the $4s$ -subshell. Hence, metallic bonds in Fe are much stronger than those in Cu.

b. $\text{Co} (Z = 27) \Rightarrow 3d^7 4s^2$, $\text{Co}^{2+} = 3d^7$ (3 unpaired electron)
 $\text{Ni} (Z = 28) \Rightarrow 3d^8 4s^2$, $\text{Ni}^{2+} = 3d^8$ (2 unpaired electron)

Hence, Ni has lower magnetic moment than Co.

EXAMPLE 6.10

Give reasons for the following features of transition metal chemistry:

- The lowest oxide of a transition metal (say, chromium, atomic number 24) is basic whereas the highest oxide is usually acidic.

- Transition metals sometimes exhibit very low oxidation states such as +1 and 0.

Sol.

- Lowest oxide of Cr is CrO which is basic. The highest oxide is CrO_3 which is acidic. (In between, Cr_2O_3 is amphoteric). Higher the oxidation state of the metal, more easily it can accept electrons and hence greater is the acidic character.
- The +1 oxidation state is shown by Cu because after loss of one electron, it acquires stable configuration of $3d^{10}$. Zero oxidation state is shown in forming metal carbonyls, e.g., $\text{Ni}(\text{CO})_4$ because π -electrons donated by the ligands are accepted into the empty d orbitals.

EXAMPLE 6.11

The $4d$ and $5d$ series of transition metals have more frequent metal-metal bonding in their compounds than do the $3d$ metals. Explain.

Sol. In the same group of d -block elements, the $4d$ and $5d$ transition element has larger size than that of $3d$ element. Thus, the valence electrons are less tightly held and hence can form metal-metal bond more frequently. (That is why melting points of $4d$ and $5d$ series as well as enthalpies of atomisation are higher than those of $3d$ series).

EXAMPLE 6.12

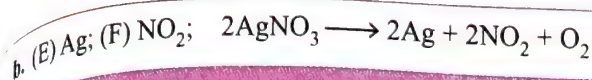
- K_2PtCl_6 is a well known compound whereas corresponding Ni compound is not known. State a reason for it.
- Most of the transition metals do not displace hydrogen from dilute acids. Why?
- Why have the transition elements high enthalpy of hydration?
- Chromium is a typical hard metal while mercury is a liquid. Explain why?

Sol.

- This is because Pt^{4+} is more stable than Ni^{4+} as the sum of four ionisation enthalpies of Pt is less than that of Ni.
- This is because most of the transition metals have negative oxidation potentials.
- This is due to their small size and large nuclear charge. This is so because when we move along any transition series, the nuclear charge increases and size decreases.
- Cr has five unpaired d electrons in the d -subshell ($3d^5 4s^1$). Hence, metallic bonds are very strong. In Hg, all the d -orbitals are fully filled ($3d^{10} 4s^2$). Hence, the metallic bonding is very weak.

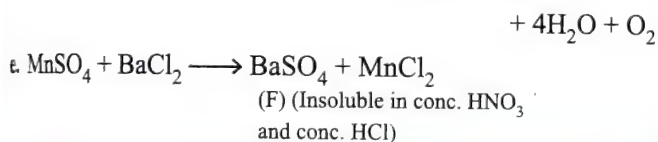
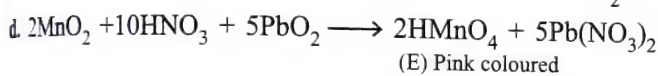
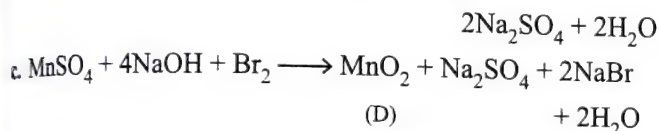
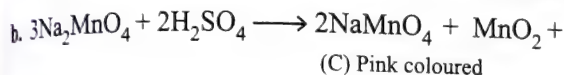
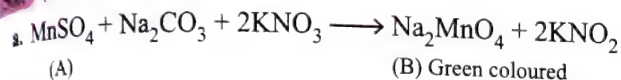
EXAMPLE 6.13

- Of the lanthanides, cerium ($Z = 58$) forms a tetrapositive ion, Ce^{4+} in aqueous solution. Why?
- The +3 oxidation states of lanthanum ($Z = 57$), gadolinium ($Z = 64$) and lutetium ($Z = 71$) are especially stable. Why?
- Why Zr and or Nb and Ta exhibit similar properties?
- Which out of the two, $\text{La}(\text{OH})_3$ and $\text{Lu}(\text{OH})_3$, is more basic and why?

**EXAMPLE 6.18**

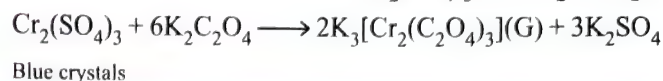
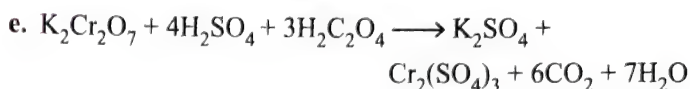
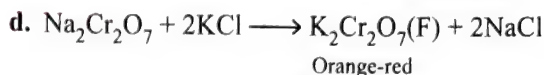
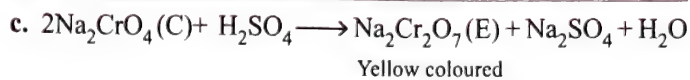
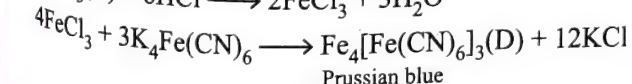
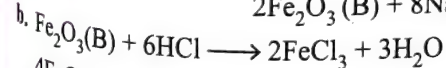
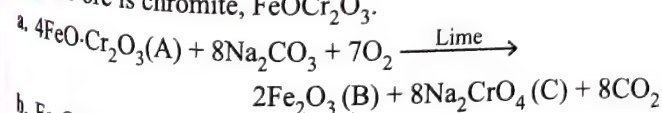
Identify A to E.

- A powdered substance (A) on treatment with fusion mixture gives a green coloured compound (B).
- The solution of (B) in boiling water on acidification with dilute H₂SO₄ gives a pink coloured compound (C).
- The aqueous solution of (A) on treatment with NaOH and Br₂-water gives a compound (D).
- A solution of (D) in conc. HNO₃ on treatment with lead peroxide at boiling temperature produced a compound (E) which was of the same colour as that of (C).
- A solution of (A) in dilute HCl on treatment with a solution of barium chloride gave a white precipitate of compound (F) which was insoluble in conc. HNO₃ and conc. HCl.

Sol. (A) is MnSO₄**EXAMPLE 6.19**

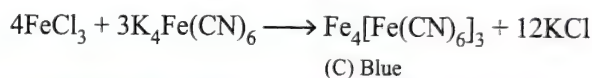
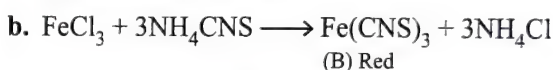
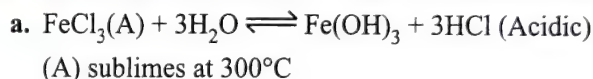
Identify A to G.

- An ore (A) on roasting with sodium carbonate and lime in the presence of air gives two compounds, (B) and (C).
- The solution of (B) in conc. HCl on treatment with potassium ferrocyanide gives a blue colour or precipitate of compound (D).
- The aqueous solution of (C) on treatment with conc. H₂SO₄ gives a yellow coloured compound (E).
- Compound (E) when treated with KCl gives an orange-red compound (F) which is used as an oxidising reagent.
- The solution of (F) on treatment with oxalic acid and then with an excess of potassium oxalate gives blue crystals of compound (G).

Sol. The ore is chromite, FeOCr₂O₃.**EXAMPLE 6.20**

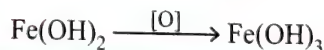
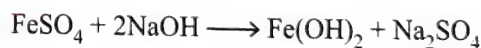
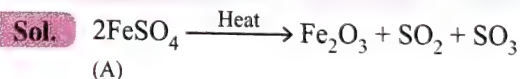
Identify A to C.

- An aqueous solution of a compound (A) is acidic towards litmus and (A) is sublimed at about 300°C.
- (A) on treatment with an excess of NH₄CNS gives a red coloured compound (B) and on treatment with a solution of K₄Fe(CN)₆ gives a blue coloured compound (C).

Sol. (A) is FeCl₃. It gives red colour of Fe(CNS)₃ with NH₄CNS and chromyl chloride test for Cl⁻ ion. The reactions are:**EXAMPLE 6.21**

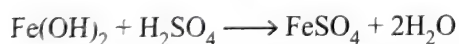
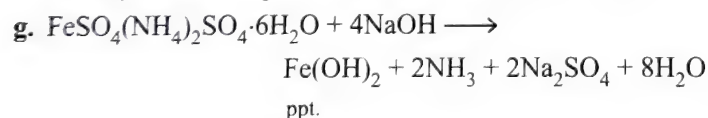
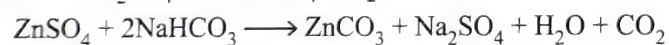
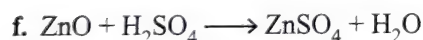
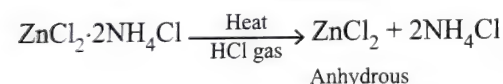
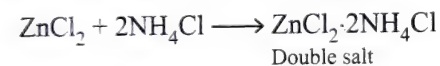
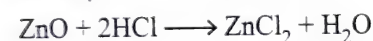
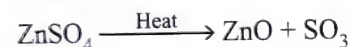
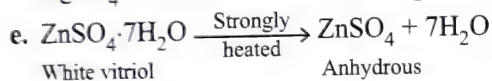
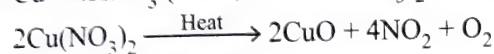
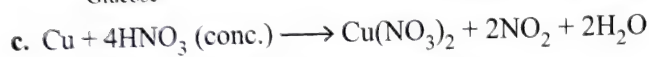
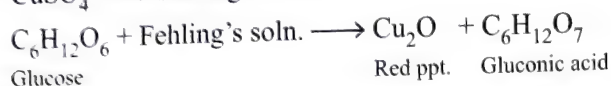
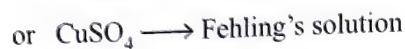
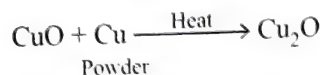
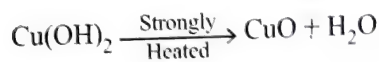
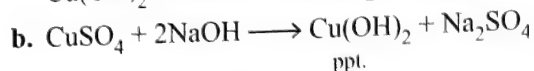
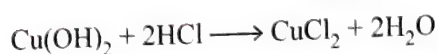
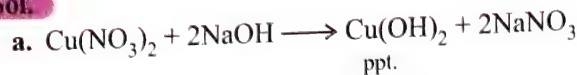
Identify A.

- Compound (A) on strong heating gives two oxides of sulphur.
- On adding aqueous NaOH solution to its aqueous solution, a dirty green precipitate is obtained which starts brown on exposure to air.

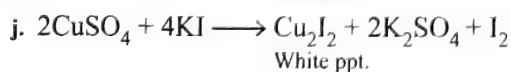
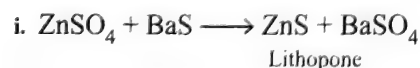
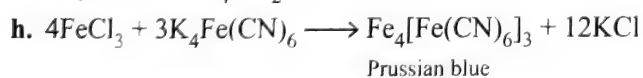
**EXAMPLE 6.22**

How the following conversions are made? Explain only by giving chemical equations.

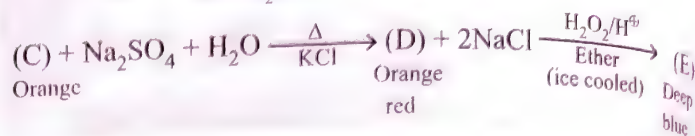
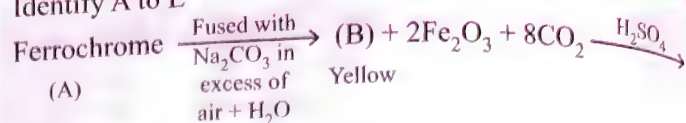
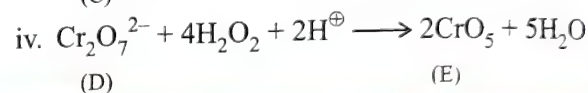
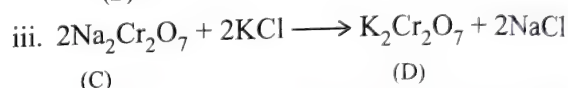
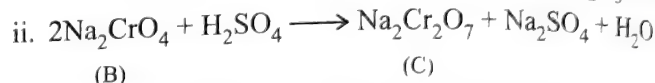
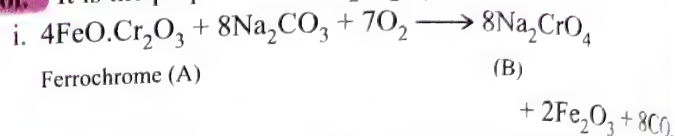
- Copper chloride from copper nitrate.
- Cuprous oxide from copper sulphate.
- Cuprous oxide from copper.
- Mercuric chloride from mercuric sulphate.
- Anhydrous ZnCl₂ from white vitriol.
- Zinc carbonate from zinc oxide.
- Ferrous sulphate from ferrous ammonium sulphate.
- Prussian blue from K₄Fe(CN)₆.
- Lithopone from white vitriol.
- Cuprous iodide from copper sulphate.

Sol.

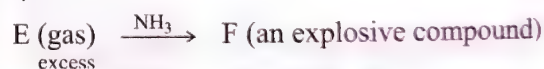
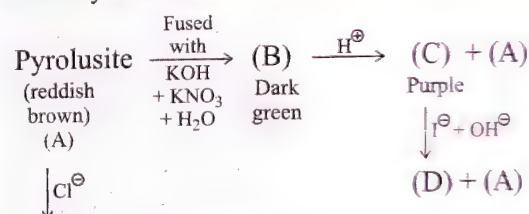
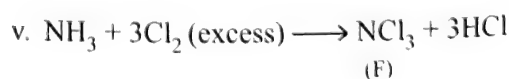
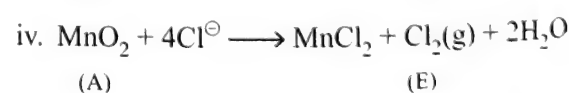
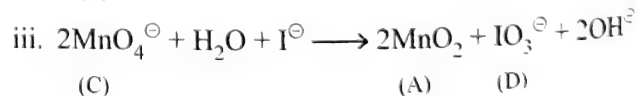
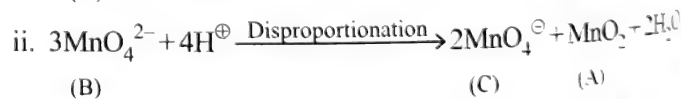
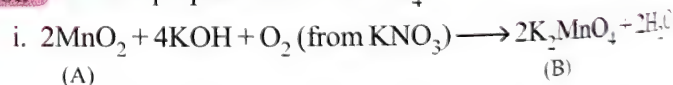
solution is put to crystallisation when crystals of ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, are obtained.

**EXAMPLE 6.23**

Identify A to E

**Sol.** It is the preparation of $\text{K}_2\text{Cr}_2\text{O}_7$ **EXAMPLE 6.24**

Identify A to F:

**Sol.** It is the preparation of KMnO_4 .

Exercises

Single Correct Answer Type

General Properties and Electronic Configuration

1. In general, the melting and boiling points of transition metals

- (1) Increases gradually across the period from left to right
- (2) Decreases gradually across the period from left to right
- (3) First increases till the middle of the period and then decreases towards the end
- (4) First decreases regularly till the middle of the period and then increases towards the end

2. Which metal has the highest melting point?

- (1) Pt (2) W
- (3) Pd (4) Au

3. Which metal has the lowest melting point?

- (1) Cs (2) Na
- (3) Hg (4) Sn

4. The inner transition elements are the element which the added electrons go to

- (1) $(n-1)$ d -orbitals
- (2) $(n-2)$ f -orbitals
- (3) $(n-1)$ d -orbitals and $(n-1)$ f -orbitals
- (4) $(n-1)$ d -orbitals and ns orbitals.

5. The electronic configuration of actinides **cannot be** assigned with degree of certainty because of

- (1) Small energy difference between $5f$ and $6d$ levels
- (2) Overlapping of inner orbitals
- (3) Free movement of electrons over all the orbitals
- (4) None of above

6. Among the following series of transition metal ions, the one where all metal ions have $3d^2$ electronic configuration is

- (1) Ti^{3+} , V^{2+} , Cr^{3+} , Mn^{4+} (2) Ti^{4+} , V^{3+} , Cr^{4+} , Mn^{5+}
- (3) Ti^{4+} , V^{3+} , Cr^{2+} , Mn^{3+} (4) Ti^{2+} , V^{3+} , Cr^{4+} , Mn^{5+}

7. The first ionisation energies of the elements of the first transition series ($Ti \rightarrow Cu$)

- (1) Increases as the atomic number increases
- (2) Decreases as the atomic number increases
- (3) Do not show any change as the addition of electrons takes place in the inner $(n-i)$ d -orbitals
- (4) Increases from Ti to Mn and then decreases from Mn to Cu

8. Which has the largest radius?

- (1) Co^{3+} (2) Mn^{3+}
- (3) Fe^{3+} (4) Cr^{3+}

9. The atomic number of V , Cr , Mn and Fe are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionisation enthalpy?

- (1) V (2) Cr
- (3) Mn (4) Fe

10. The first ionisation energies of the elements of the transition series

- (1) Increase as the atomic number increases
- (2) Decrease as the atomic number increases
- (3) Do not show any change as the addition of electron takes place in the inner $(n-1)$ d -orbitals
- (4) None of the above

11. Among $3d$ transition series the IE

- (1) Increases regularly in moving from left to right
- (2) Decreases regularly in moving from left to right
- (3) Remains constant within the period
- (4) Increases gradually within the period but the relative increase is not sharp

12. Which of the following is the most suitable description of transition elements?

- (1) Low melting points
- (2) No catalytic activity
- (3) Show variable oxidation states
- (4) Exhibit inert pair effect

13. Select the **incorrect** statement:

- (1) The melting point of Mn is lower than that of Cr and Fe in $3d$ series.
- (2) The melting point of Tc is higher than that of Mo but lower than that of Ru in $4d$ series.
- (3) The melting point of W (tungsten) is highest in $5d$ series.
- (4) The order of melting points of $3d$, $4d$ and $5d$ series is: $5d > 4d > 3d$

14. Select the **incorrect** statement:

- (1) The atomic radii of $4d$ series are larger than those of $3d$ series
- (2) The atomic radii of $4d$ and $5d$ series are almost same.
- (3) Stability of the M^{3+} ions in aqueous solution is: $Sc^{3+} > Cr^{3+} > Fe^{3+} > Co^{3+}$
- (4) Basic strength of the hydroxides is: $La(OH)_3 < Y(OH)_3 < Sc(OH)_3$

15. Select the **incorrect** statement:

- (1) The higher oxidation state for d -block elements is most stable with F
- (2) The bond strength order of the following ions is: $Zn^{2+} > Hg^{2+} > Cd^{2+}$
- (3) The ionic size of the following ions is: $Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+}$
- (4) Mn_2O_7 exists but MnF_7 does not

16. Select the correct statement:

- (1) Zero and negative oxidation state of d -block metal ion is possible in their complex compound.
- (2) Aqueous Cu^{\oplus} cation undergo disproportionation due to hydration energy of Cu^{2+} is higher than that of Cu^{\oplus} which compensates first ionisation energy of Cu .

- (3) Zn gives H_2 gas with dil. HCl and dil. H_2SO_4 but gives $NO_2(g)$ with dil. HNO_3
 (4) Covalent character is: $HgCl_2 > CdCl_2 > ZnCl_2$

Colour

17. Which of the following compound is not coloured?
 (1) Copper(II) sulphate (2) Zinc(II) chloride
 (3) Chromium(II) sulphate (4) Manganese(II) oxalate
18. Amongst, $NiCl_4^{2-}$, Cu_2Cl_2 , ScF_6^{3-} and CoF_6^{3-} , the coloured species are:
 (1) ScF_6^{3-} and Cu_2Cl_2 (2) ScF_6^{3-} and CoF_6^{3-}
 (3) Cu_2Cl_2 and $NiCl_4^{2-}$ (4) CoF_6^{3-} , $NiCl_4^{2-}$
19. $K_3[Fe(CN)_6]$ is used in the detection of Fe^{2+} ion, which gives a blue colour solution. This colour is due to the formation of:
 (1) $Fe_4[Fe(CN)_6]_3$ (2) $Fe_3[Fe(CN)_6]_2$
 (3) $Fe[Fe(CN)_6]$ (4) $K_2Fe[Fe(CN)_6]$

Magnetic Properties

20. Which of the following contains the maximum number of unpaired electrons?
 (1) $TiCl_3$ (2) $MnCl_3$
 (3) $FeSO_4$ (4) $CuSO_4$
21. Among the following pairs of ions, the lower oxidation state in aqueous solution is more stable than the other in
 (1) Ti^{\oplus} , Ti^{3+} (2) Cu^{\oplus} , Cu^{2+}
 (3) Cr^{2+} , Cr^{3+} (4) V^{2+} , VO^{2+}
22. Within each transition series, the oxidation states
 (1) Decreases regularly in moving from left to right
 (2) First increases till the middle of period and then decreases
 (3) First decreases till the middle of period and then increases
 (4) None of the trend is correct
23. In which of the following complexes the metal ion is in zero oxidation state?
 (1) $[Cu(NH_3)_4]Cl_2$ (2) $Zn_2[Fe(CN)_6]$
 (3) $Mn_2(CO)_{10}$ (4) $[Ag(NH_3)_2]Cl$
24. In general the order of reactivity of halogens with transition metals is
 (1) $F_2 > Cl_2 > Br_2 > I_2$ (2) $F_2 < Cl_2 < Br_2 < I_2$
 (3) $F_2 < Cl_2 > Br_2 < I_2$ (4) $F_2 > I_2 > Br_2 > Cl_2$
25. Select the incorrect statement:
 (1) Orbital angular momentum for first series of transition metals is of no significance.
 (2) The observed paramagnetism in 4f-block elements is due to both orbital motion of the electron and its spinning around its axis.
 (3) Highest paramagnetism in 3d series in +1 oxidation state is shown by Mn^{+1} .
 (4) Highest paramagnetism in +2 oxidation state in 4d series is shown by Mo^{+2} .
26. Out of the following, how many of them have magnetic moment value of $\sqrt{48}$ BM
 (i) Cr, (ii) Re, (iii) W, (iv) Mo, (v) Mn^{+1} , (vi) Tc^{+1} , (viii) Fe^{+3}
 (1) 5 (2) 4
 (3) 3 (4) 2
- Chemical Characteristics, $KMnO_4$ and $K_2Cr_2O_7$**
27. Which of the following cannot reduce the acidified solution of permanganate?
 (1) $(COOH)_2$ (2) H_2
 (3) Nascent hydrogen (4) Fe^{2+} ions
28. Which of the following can be employed for the conversion of potassium manganate to potassium permanganate?
 (1) O_3 (2) Cl_2
 (3) Electrolysis (4) All
29. The blue colour produced on adding H_2O_2 to acidified $K_2Cr_2O_7$ is due to the formation of
 (1) CrO_5 (2) Cr_2O_3
 (3) CrO_4^{2-} (4) CrO_3
30. The equilibrium $Cr_2O_7^{2-} \rightleftharpoons 2CrO_4^{2-}$
 (1) Exists in acidic medium
 (2) Exists in basic medium
 (3) Exists in neutral medium
 (4) It does not exist
31. Which of the following compounds is used as the starting material for the preparation of potassium dichromate?
 (1) $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ (Chrome alum)
 (2) $PbCrO_4$ (Chrome yellow)
 (3) $FeCr_2O_4$ (Chromite)
 (4) $PbCrO_4 \cdot PbO$ (Chrome red)
32. The image on an exposed and developed photographic film is due to
 (1) AgBr (2) $[Ag(C_2O_3)_2]^{3+}$
 (3) Ag (4) Ag_2O
33. During titration, H_2SO_4 is preferably used over HCl and HNO_3 to make the solution acidic because
 (1) H_2SO_4 is a strong oxidising agent and it reacts with $KMnO_4$ during titration
 (2) Some $KMnO_4$ is consumed during the reaction with H_2SO_4
 (3) H_2SO_4 does not react with $KMnO_4$ or the reducing agent used
 (4) H_2SO_4 can turn colourless $KMnO_4$ to pink at the end point
34. When $KMnO_4$ is added to oxalic acid, the decolourisation is slow in the beginning 'but becomes instantaneous after sometime because
 (1) Mn^{2+} acts as autocatalyst
 (2) CO_2 is formed as the product
 (3) Reaction is exothermic
 (4) MnO_4^{\ominus} catalyses the reaction
35. Which of the following oxides of manganese is amphoteric?
 (1) MnO_2 (2) Mn_2O_3
 (3) Mn_2O_7 (4) MnO
36. Number of moles of $K_2Cr_2O_7$ reduced by one mole of Sn^{2+} ion is
 (1) 1/3 (2) 3
 (3) 1/6 (4) 6

37. CrO_3 dissolves in aqueous NaOH to give
 (1) CrO_4^{2-} (2) $\text{Cr}(\text{OH})_3$
 (3) $\text{Cr}_2\text{O}_7^{2-}$ (4) $\text{Cr}(\text{OH})_2$
38. An explosion takes place when conc. H_2SO_4 is added to KMnO_4 . Which of the following is formed?
 (1) Mn_2O_7 (2) MnO_2
 (3) MnSO_4 (4) Mn_2O_3
39. Formation of interstitial compound makes the transition metal
 (1) More soft (2) More ductile
 (3) More metallic (4) More hard
40. Acidic MnO_4^- solution oxidises H_2O_2 and faintly alkaline MnO_4^- solution oxidises $\text{S}_2\text{O}_3^{2-}$ respectively to:
 (1) O_2 , $\text{S}_4\text{O}_6^{2-}$ (2) O_2 , $\text{S}_2\text{O}_3^{2-}$
 (3) H_2O , $\text{S}_4\text{O}_6^{2-}$ (4) H_2O , $\text{S}_2\text{O}_3^{2-}$
41. Select the correct statement:
 (1) Titration of KMnO_4 is carried out in presence of HCl .
 (2) Titration of KMnO_4 is carried out in presence of HNO_3 .
 (3) Titration of KMnO_4 is carried out in presence of H_2SO_4 .
 (4) All
42. MnO_4^- oxidises I^- ion in acidic medium and MnO_4^- is reduced respectively to:
 (1) I_2 , Mn^{2+} (2) IO_3^- , Mn^{2+}
 (3) I_2 , MnO_2 (4) IO_3^- , MnO_2
43. MnO_4^- oxidises I^- in basic medium and MnO_4^- is reduced respectively to:
 (1) I_2 , Mn^{2+} (2) IO_3^- , Mn^{2+}
 (3) I_2 , MnO_2 (4) IO_3^- , MnO_2
44. Select incorrect statement:
 (1) H_2O_2 oxidises ice-cooled acidic $\text{Cr}_2\text{O}_7^{2-}$ or CrO_4^{2-} in ether to a compound having butterfly structure.
 (2) The ethereal layer turn red in colour due to the formation of $[\text{CrO}(\text{O}_2)_2]$.
 (3) The colour fades away gradually due to decomposition of $[\text{CrO}(\text{O}_2)_2]$ to Cr^{3+} and O_2 .
 (4) The oxidation state of Cr in butterfly structure is +6.
45. CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are interconvertible in aqueous solution and they are in equilibrium at $\text{pH} = 4$. The colour of the solution at $\text{pH} = 3$ and $\text{pH} = 8$ are respectively.
 (1) Yellow, Red (2) Red, Yellow
 (3) Orange red, Yellow (4) Yellow, Orange red
46. Acidified MnO_4^- solution does not oxidise.
 (1) F^- , NO_3^- (2) $\text{C}_2\text{O}_4^{2-}$, S^{2-}
 (3) $\text{C}_2\text{O}_4^{2-}$, NO_3^- (4) S^{2-} , F^-
47. The lanthanide contraction relates to
 (1) Atomic radii
 (2) Atomic as well as M^{3+} radii
 (3) Valence electrons
 (4) Oxidation states
48. The properties of Zr and Hf are similar because
 (1) Both belong to d-block
 (2) Both belong to same group of the periodic table
 (3) Both have similar radii
 (4) Both have same number of electrons
49. Cerium shows oxidation state of +4 because
 (1) It resembles alkali metals
 (2) It has very low IE
 (3) It has tendency to attain noble gas configuration
 (4) It has tendency to attain f^0 configuration
50. Which of the two have almost similar size
 (1) $_{22}\text{Ti}$ and $_{40}\text{Zr}$ (2) $_{41}\text{Nb}$ and $_{73}\text{Ta}$
 (3) $_{39}\text{Y}$ and $_{57}\text{La}$ (4) $_{20}\text{Ca}$ and $_{31}\text{Ir}$
51. Which of the following statement is **not correct**?
 (1) $\text{La}(\text{OH})_3$ is less basic than $\text{Lu}(\text{OH})_3$
 (2) In lanthanide series ionic radius of Ln^{3+} ions decreases
 (3) La is actually an element of transition series rather than lanthanide series
 (4) Atomic radii of Zr and Hf are same because of lanthanide contraction
52. The reason for the stability of Gd^{3+} ion is
 (1) 4f subshell—half filled
 (2) 4f subshell—completely filled
 (3) Possesses the general electronic configuration of noble gases.
 (4) 4f-subshell empty.
53. Arrange (I) Ce^{3+} , (II) La^{3+} , (III) Pm^{3+} and (IV) Yb^{3+} in increasing order of their ionic radii.
 (1) $\text{IV} < \text{III} < \text{I} < \text{II}$ (2) $\text{I} < \text{IV} < \text{III} < \text{II}$
 (3) $\text{IV} < \text{III} < \text{II} < \text{I}$ (4) $\text{III} < \text{II} < \text{I} < \text{IV}$
54. The radius of La^{3+} ($Z = 57$) is 106 pm. Which one of the following given values will be closest to the radius of Lu^{3+} ($Z = 71$)?
 (1) 160 pm (2) 140 pm
 (3) 106 pm (4) 85 pm
55. Lanthanides and actinides resemble in
 (1) Electron configuration (2) Oxidation state
 (3) Ionisation energy (4) Formation of complexes
56. Misch metal is
 (1) An alloy of aluminium
 (2) A mixture of chromium and lead chromate
 (3) An alloy of lanthanoid metals
 (4) An alloy of copper
57. In aqueous solutions Eu^{2+} acts as
 (1) An oxidising agent (2) A reducing agent
 (3) Can act either of these (4) Can act as redox agent
58. Which transition metal has lowest density?
 (1) Sc (2) Ti
 (3) Zn (4) La
59. Among the transition elements the element with lowest melting point belongs to

- (1) Group 3 (2) Group 11
(3) Group 6 (4) Group 12
60. The stability of particular oxidation state of a metal in aqueous solution is determined by
(1) Enthalpy of sublimation of the metal
(2) Ionisation energy
(3) Enthalpy of hydration of the metal ion
(4) All of these
61. Which of the following is not a condition for complex formation?
(1) Small atomic size
(2) High nuclear charge
(3) Variable oxidation states
(4) Availability of vacant *d* orbitals
62. Which is not amphoteric?
(1) Al^{3+} (2) Cr^{3+}
(3) Fe^{3+} (4) Zn^{2+}
63. Both acid and base may react with which of the following oxides?
(1) CaO (2) Na_2O_2
(3) ZnO (4) Mn_3O_4
64. Coinage metals show the properties of
(1) Typical elements (2) Normal elements
(3) Transitional elements (4) Inert elements
65. When $(\text{NH}_4)_2\text{CrO}_2\text{O}_7$ is heated, the gas evolved is
(1) N_2 (2) NO_2
(3) O_2 (4) Na_2O
66. Which of the following oxides of Cr is amphoteric
(1) CrO_2 (2) Cr_2O_3
(3) CrO_5 (4) CrO_3
67. Select the incorrect statement:
(1) Actinides shows large number of oxidation states than that of corresponding lanthanides
(2) Pyrophoric alloy is 3% misch metal mixed with Mg
(3) The size of lanthanides M^{3+} ions increases as the atomic number of M increases
(4) Electronic spectra of lanthanide show very broad bands
68. Select the incorrect statement:
(1) Sphalerite is an ore of zinc
(2) Terbium (Tb) has $4f^9 6s^2$ and Gadolinium (Gd) has $4f^7 5s^1 6s^2$ electronic configuration. The spin magnetic moment of Tb^{3+} is greater than Gd^{3+}
(3) All actinides have high densities except Th and Am.
(4) Monazite is an ore of thorium.
69. Select incorrect statement:
(1) Actinides with $5f^1$, $5f^5$ and $5f^8$ electronic configuration are not known.
(2) Lanthanides with $4f^2$ and $4f^8$ electronic configuration are not known.
(3) Lanthanoid compounds are less basic than actinoid compounds.
(4) Lanthanoid compounds have more tendency towards complex formation.

Compounds of Transition Elements

Iron

70. Important ore of iron is
(1) Garnierite (2) Pentlandite
(3) Haematite (4) Smaltite
71. A compound of iron exists as a dimer in vapour state. It is hygroscopic in nature and dissolves in water giving brown acidic solution. The compound is
(1) Fe_3O_4 (2) FeSO_4
(3) FeCl_3 (4) FeO_2
72. Which among FeO and Fe_2O_3 is more basic?
(1) FeO
(2) Fe_2O_3
(3) Both have same basic strength
(4) None of them is basic
73. The colour of FeF_3 is
(1) Brown (2) Red brown
(3) Light green (4) White
74. Iron is obtained on a large scale from Fe_2O_3 by
(1) Reduction with Al (2) Smelting with carbon
(3) Calcination (4) Water gas
75. The deep red colour of $\text{Fe}(\text{SCN})_3$ and $\text{Fe}(\text{SCN})_4^-$ is destroyed by addition of
(1) F^- (2) CN^-
(3) SCN^- (4) Fe^3+

Copper

76. On heating copper nitrate strongly the compound obtained is
(1) Copper (2) Copper oxide
(3) Copper nitrite (4) Copper nitride
77. Which of the following is fool's gold?
(1) CuFeS_2 (2) $\text{Cu}(\text{OH})_2$
(3) $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ (4) Cu_2S
78. Bordeaux mixture consists of lime and
(1) FeSO_4 (2) CuSO_4
(3) $\text{Cu}(\text{NO}_3)_2$ (4) AgNO_3
79. In vapour state $\text{Cu}(\text{NO}_3)_2$ and $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ exist as
(1) Dimer, monomer
(2) Monomer, dimer
(3) Monomer, monomer
(4) Dimer, Dimer
80. Which compound is formed when iron reacts with carbon?
(1) FeC_2 (2) Fe_3C
(3) FeC_3 (4) Fe_2C

Silver:

81. Which of the following is known as WORM SILVER?
(1) AgCl
(2) A specific horn, type article made of silver
(3) Ag_2S
(4) PbS containing traces of Ag_2S

It is always advisable not to cover egg yolk or mustard with silver cutlery because

- (1) Silver reacts with water of egg yolk to form AgOH
- (2) Silver reacts with sulphur of egg yolk forming black Ag_2S
- (3) Silver reacts with egg yolk forming Ag_2SO_4 which is a poisonous substance
- (4) Silver attracts UV light of the atmosphere, thereby spoiling the food.

Silver halides are used in photography because they are

- (1) Photosensitive
- (2) Soluble in hyposolution
- (3) Soluble in NH_4OH
- (4) Insoluble in acids

Which of the following is false?

- (1) Molten lead and zinc are miscible.
- (2) Silver is more soluble in molten zinc than lead.
- (3) Zinc-silver alloy is volatile.
- (4) Zinc-silver alloy is heavier and gets solidified later than lead.

AgNO_3 gives red ppt. with

- (1) NaI
- (2) KCl
- (3) NaNO_3
- (4) Na_2CrO_4

Gold

Percentage of gold in 21.6 carat gold is

- (1) 21.8%
- (2) 90%
- (3) 10%
- (4) 70%

Gold dissolves in aqua regia forming

- (1) $\text{Au}(\text{NO}_3)_2$
- (2) $\text{H}[\text{AuCl}_4]$
- (3) AuCl
- (4) AuNO_3

The process of extraction of Au and Ag ores is based on their solubility in

- (1) NH_3
- (2) HCl
- (3) HNO_3
- (4) KCN

Mercury

Which of the following is used as purgative in medicine?

- (1) ZnCl_2
- (2) HgCl_2
- (3) Hg_2Cl_2
- (4) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

The roasting of HgS in air produces

- (1) HgO
- (2) HgSO_3
- (3) HgSO_4
- (4) Hg

Which of the following is used as a white pigment?

- (1) ZnO
- (2) Na_2ZnO_2
- (3) ZnS
- (4) ZnCO_3

Mercury (I) chloride sublimes, when this compound is heated and the vapours it gives off are cooled the substance collected consists of

- (1) Mercury (II) chloride
- (2) Mercury (I) and Mercury (II), chlorides
- (3) Mercury (II) chloride and mercury
- (4) Mercury

Zinc

93. White vitriol is

- (1) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- (2) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
- (3) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
- (4) $\text{NiSO}_4 \cdot 5\text{H}_2\text{O}$

94. When zinc reacts with very dilute nitric acid it produces

- (1) NO
- (2) NH_4NO_3
- (3) NO_2
- (2) H_2

95. Lithopone is a mixture of

- (1) ZnSO_4 , BaSO_4
- (2) ZnS , BaSO_4
- (3) ZnCO_3 , BaSO_3
- (4) ZnS , Na_2SO_4

Miscellaneous Compounds

96. Iron is rendered passive by treatment with

- (1) H_2SO_4
- (2) H_3PO_4
- (3) HCl
- (4) conc. HNO_3

97. Nitriding is a process of hardening steel by treating it in an atmosphere of

- (1) NH_3
- (2) O_3
- (3) N_2
- (4) H_2O

98. Which of the following is used for joining the broken pieces of glass and stones?

- (1) Haematite
- (2) Sindoor
- (3) Massicot
- (4) German silver

99. Which method is based on distribution principle?

- (1) Mond's process
- (2) Plattner's principle
- (3) Glower's process
- (4) Parke's process

100. Which of the following statements is wrong?

- (1) An acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$ liberates iodine from iodides
- (2) In acidic solution dichromate ions are converted to chromate ions
- (3) Ammonium dichromate on heating undergo exothermic decomposition to give Cr_2O_3
- (4) Potassium dichromate is used as a titrant for Fe^{2+} ions

101. When H_2S gas is passed through an orange red solution (X), the solution turns milky. When an alkali is added to this orange red solution it turns yellow and on acidifying this yellow solution again turns orange red. X is

- (1) K_2CrO_4
- (2) KMnO_4
- (3) $\text{Na}_2\text{Cr}_2\text{O}_7$
- (4) $\text{K}_2\text{Cr}_2\text{O}_7$

102. Which of the following statements is incorrect?

- (1) Basic copper carbonate is $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
- (2) On strong heating potassium dichromate decomposes with evolution of oxygen
- (3) CuS is white in colour
- (4) KMnO_4 exists as dark purple black prismatic crystals

103. A man made white silvery metal, radioactive in nature has a strong tendency to form oxocations and complexes. It is used as a nuclear fuel in atomic reactors. The metal is a

- (1) Lanthanide
- (2) Actinide
- (3) Transition metal
- (4) Representative element

104. From a solution of CuSO_4 , the metal used to recover copper is

- (1) Na (2) Ag
(3) Hg (4) Fe
105. Iron, once dipped in concentrated H_2SO_4 , does not displace copper from copper sulphate solution, because
(1) It is less reactive than copper
(2) A layer of sulphate is deposited on it
(3) An inert layer of iron oxide is deposited on it
(4) All valence electrons of iron are consumed
106. Which of the following ions will finally give a black precipitate with Ag^+ ion?
(1) SO_3^{2-} (2) Br^-
(3) CrO_4^{2-} (4) $\text{S}_2\text{O}_3^{2-}$
107. The compound which gives oxygen on moderate heating is
(1) Zinc oxide (2) Mercuric oxide
(3) Aluminium oxide (4) Ferric oxide
108. Identify the statement which is not correct regarding CuSO_4
(1) It reacts with KI to give iodine
(2) It reacts with KCl to give Cu_2Cl_2
(3) It reacts with NaOH and glucose to give Cu_2O
(4) It gives CuO on strong heating in air
109. KI and CuSO_4 solutions when mixed give
(1) $\text{CuI}_2 + \text{K}_2\text{SO}_4$ (2) $\text{Cu}_2\text{I}_2 + \text{K}_2\text{SO}_4$
(3) $\text{K}_2\text{SO}_4 + \text{Cu}_2\text{I}_2 + \text{I}_2$ (4) $\text{K}_2\text{SO}_4 + \text{CuI}_2 + \text{I}_2$
110. Bordeaux used a fungicide is a mixture of
(1) $\text{CuSO}_4 + \text{Ca}(\text{OH})_2$ (2) $\text{CaSO}_4 + \text{Cu}(\text{OH})_2$
(3) $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ (4) $\text{CuO} + \text{CaO}$
111. Mercury is the only metal which is liquid at 0°C . This is due to its
(1) Very high ionisation energy and weakly metallic bond
(2) Low ionisation potential
(3) High atomic weight
(4) High vapour pressure
112. Which one of the following is false for Hg?
(1) It can evolve hydrogen from H_2S
(2) It is metal
(3) It has high specific heat
(4) It is less reactive than hydrogen
113. Which compound is volatile on heating?
(1) MgCl_2 (2) HgCl_2
(3) ZnCl_2 (4) None of these
114. Which one of the following pairs of substances on reaction will not evolve H_2 gas?
(1) Iron and $\text{H}_2\text{SO}_4(\text{aq})$
(2) Iron and steam
(3) Copper and $\text{HCl}(\text{g})$
(4) Sodium and ethyl alcohol
115. Which of the following is not the characteristic of zinc?
(1) It is volatile metal
(2) It dissolves in alkali forming sodium zincate
(3) It is brittle at very high temperatures
(4) Zinc dust is used as a reducing agent
116. The correct formula of permanganic acid is
(1) HMnO_4 (2) HMnO_5
(3) H_2MnO_4 (4) H_2MnO_3
117. Which of the following species undergo non-redox thermal decomposition on heating.
(1) SnSO_4 (2) $\text{H}_2\text{C}_2\text{O}_4$
(3) Na_2HPO_4 (4) FeSO_4
118. Water soluble salt (X) is heated into three products A, B and C. Products B and C are two different paramagnetic gases (A) is red in hot solution. The salt (X) is:
(1) FeC_2O_4 (2) $\text{Hg}(\text{NO}_3)_2$
(3) $\text{Pb}(\text{NO}_3)_2$ (4) ZnSO_4
119. Metal $\xrightarrow[\text{HNO}_3]{\text{dil.}}$ Colourless solution $\xrightarrow{\text{aq. NaOH}}$
(M) $\xrightarrow[\text{NaOH (aq)}]{\text{excess}}$ Colourless solution
white ppt. $\xrightarrow{\text{H}_2\text{S}}$ white ppt.
Metal (M) is:
(1) Sn (2) Zn
(3) Pb (4) Mg
120. Select incorrect statement:
(1) Pt^{+4} compounds are relatively more stable than Ni^{+4} compounds
(2) LiAlH_4 on hydrolysis gives H_2
(3) The welding of Mg can be done in the atmosphere of helium
(4) In the reaction of S^{2-} ion, with nitroprusside ion, to form a purple coloured compound. In this reaction oxidation state of Fe changes
121. $\text{CuSO}_4(\text{aq}) \xrightarrow{\text{H}_2\text{S}} \text{A} \xrightarrow{\text{excess of KCN}} \text{B} + \text{C}$.
The product B and C respectively are:
(1) CuCN , $(\text{CN})_2$ (2) $\text{Cu}(\text{CN})_2$, K_2S
(3) $[\text{Cu}(\text{CN})_4]^{2-}$, $(\text{CN})_2$ (4) $[\text{Cu}(\text{CN})_4]^{3-}$, $(\text{CN})_2$
122. Consider the reaction,
 $2\text{CuX}_2 \xrightarrow[\text{temperature}]{\text{Room}} 2\text{CuX} + \text{X}_2$
 X^- ion is
(1) Cl^- , F^- (2) Cl^- , Br^-
(3) F^- , Br^- (4) CN^- , I^-

Multiple Correct Answers Type

General Properties and Electronic Configuration

1. d_{z^2} orbital is involved in which of the following hybridisation?
(1) sp^3d (2) dsp^3
(3) sp^3d^2 (4) d^2sp^3
2. d_{xy} , d_{yz} and d_{xz} orbitals are involved in which of the following hybridisation?
(1) dsp^2 (2) sp^3d
(3) sp^3d^2 (4) d^3sp^3

3. $d_{x^2-y^2}$ and d_{z^2} orbital is involved in which of the following hybridisation?

- (1) sp^3d^2 (2) d^2sp^3
(3) sp^3d^3 (4) d^3sp^3

4. $d_{x^2-y^2}$ orbital is involved in which of the following hybridisation?

- (1) sp^3d (2) sp^3d^2
(3) sp^3d^3 (4) None of these

5. Which of following is/are correctly matched?

- (1) d-block element : electronic configuration is $ns^{0-2}(n-1)d^{1-10}$
(2) p-block element : electronic configuration is $ns^{1-2}np^{1-6}$
(3) s-block element : electronic configuration is ns^{1-2}
(4) Ce : f-block's first member.

6. Which of the following is false?

- (1) $Cr^{2+}_{(g)}$ ion has greater magnetic moment as compared to $Co^{3+}_{(g)}$.
(2) The magnitude of ionisation potential of iron anion (monoanion) would be equal to electron gain enthalpy of iron.
(3) Lanthanoids contraction is cause of lower IE of Pb than Sn.
(4) If successive ionisation energy are 332, 738, 849, 4080, 4958 (in kJ/mol). Then this element can be of 15th group.

7. Which of the following represents the incorrect order of the properties indicated?

- (1) $Ni^{2+} > Cr^{2+} > Fe^{2+} > Mn^{2+}$ (size)
(2) $Sc > Ti > Cr > Mn$ (size)
(3) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$ (unpaired electron)
(4) $H_3AsO_4 > H_3PO_4$ (acidic strength order)

8. What will be the correct representation of quantum numbers for the last electron entered into Ce?

n	l	m	s
(1) 4	3	-3	-1/2
(2) 4	3	0	-1/2
(3) 4	2	-3	+1/2
(4) 4	3	+2	-1/2

9. The ability of d-block elements to form complexes is due to:

- (1) Small and highly charged ions
(2) Vacant low energy orbitals to accept lone pair of electrons from ligands
(3) Low polarising power of cation
(4) None is correct

10. A transition element X has a configuration $3d^4$ in its +3 oxidation state. Its atomic number is not

- (1) 25 (2) 26
(3) 22 (4) 19

11. The transition metals which do not form amalgams are

- (1) Zn (2) Fe
(3) Cd (4) Pt

12. Transition elements have greater tendency to form complexes because

- (1) They have vacant d-orbitals
(2) They have large size
(3) They show variable oxidation state
(4) They have two electrons in their outermost shells.

13. Which out of the following belong to 3d-series?

- (1) Copper (2) Cobalt
(3) Gold (4) Silver

14. The elements which exist in the liquid state at room temperature are

- (1) Na (2) Br_2
(3) Hg (4) Ga

15. Which of the following represents the correct order of the properties indicated?

- (1) $Ni^{2+} > Cr^{2+} > Fe^{2+} > Mn^{2+}$ (size)
(2) $Sc > Ti > Cr > Mn$ (size)
(3) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$ (unpaired electron)
(4) $Cr^{3+} > Cr^{2+}$ (magnetic moment)

16. The correct statement for d-block element is

- (1) It shows magnetic property.
(2) It has variable valency.
(3) It has tendency of formation of coloured ions.
(4) It has complete d-orbitals.

17. Which is/are true statement?

- (1) Ions of d-block elements are coloured due to d-d transition.
(2) Ions of f-block elements are coloured due to f-f transition.
(3) $[Sc(H_2O)_6]^{3+}$, $[Ti(H_2O)_6]^{4+}$ are coloured complexes.
(4) Cu^{\oplus} is colourless ion.

18. Select the correct statements:

- (1) Oxides of transition metals are highly coloured (generally black).
(2) Alloy of transition metal has often high melting points.
(3) Oxides of transition elements are insoluble in water.
(4) Existence of Mn_2O_7 is due to ability of oxygen to form $\pi\pi$ - $\pi\pi$ multiple bonds to Mn

19. Select the correct statements:

- (1) Mn^{3+} and Cr^{3+} are violet in colour.
(2) Melting points of alloys is less than their individual metals.
(3) Order of acidic character of oxides of Mn.
 $Mn_2O_7 > MnO_2 > Mn_2O_3 > Mn_3O_4 > MnO$.
(4) Mn^{\oplus} , Re^{+1} and Mn^{2+} have 6 unpaired e^- 's

20. Select the correct statements:

An elements of 3d transition series shows two oxidation states x and y, differ by two units then.

- (1) Compounds in O.S., x are ionic if $x > y$
(2) Compounds in O.S., y are covalent if $x < y$
(3) Compounds in O.S., x are ionic if $x < y$
(4) Compounds in O.S., y are covalent if $y < x$

21. Select the correct statements:

- (1) "Spitting of silver" can be prevented by covering the surface of molten Ag with charcoal.
- (2) Order of paramagnetic character is: $\text{Cr} > \text{Fe} > \text{Zn}$
- (3) An alloy is a blend of metals prepared by mixing the compounds.
- (4) The melting and boiling points of Zn, Cd and Hg are high.

22. Select the correct statements:

- (1) There is a very small difference in the melting point of Cr and Zn
- (2) Chromium is a typical hard metal while mercury is a liquid.
- (3) Pt^{4+} compounds are more stable than Ni^{4+} compounds.
- (4) Ni^{2+} compounds are more stable than Pt^{2+} compounds.

Colour**23. Which one of the following ionic species will not impart colour to an aqueous solution?**

- | | |
|----------------------|--------------------------|
| (1) Ti^{4+} | (2) Cu^{\oplus} |
| (3) Zn^{2+} | (4) Cr^{3+} |

24. The colour of the transition metal ions is due to

- | | |
|----------------------------|---------------------|
| (1) $d-d$ transition | (2) Charge transfer |
| (3) Change in the geometry | (4) None |

Magnetic Properties**25. Out of $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, and $[\text{Ni}(\text{CO})_4]$: select the incorrect statement(s):**

- (1) All have identical geometry
- (2) All are paramagnetic
- (3) All are diamagnetic
- (4) $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic but $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$ are paramagnetic

 KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ **26. Which is true statement about KMnO_4 ?**

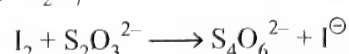
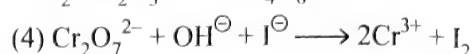
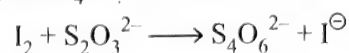
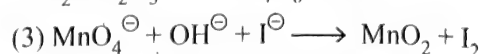
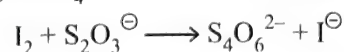
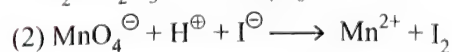
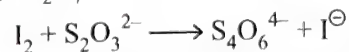
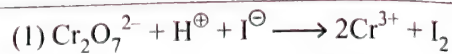
- (1) Its solution is unstable in acidic medium.
- (2) It has purple colour.
- (3) MnO_4^- changes to Mn^{2+} in basic solution.
- (4) It is self-indicator in Fe^{2+} or $\text{C}_2\text{O}_4^{2-}$ titration.

27. Potassium manganate (K_2MnO_4) is formed when

- (1) Chlorine is passed through aqueous KMnO_4 solution
- (2) Manganese dioxide is fused with potassium hydroxide in air
- (3) Formaldehyde reacts with potassium
- (4) potassium permanganate reacts with H_2SO_4

28. Cl_2 gas is obtained by various reactions select the reactions from the following(s):

- (1) $\text{KMnO}_4 + \text{conc. HCl} \xrightarrow{\Delta}$
- (2) $\text{KCl} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{conc. H}_2\text{SO}_4 \xrightarrow{\Delta}$
- (3) $\text{MnO}_2 + \text{conc. HCl} \xrightarrow{\Delta}$
- (4) $\text{KCl} + \text{F}_2 \xrightarrow{\Delta}$

29. In the iodometric estimation in the laboratory which process is involved?**30. Which reagents can convert Mn^{2+} to MnO_4^{\ominus} ?**

- | | |
|---------------------------------------------------|----------------------------------------------|
| (1) $\text{S}_2\text{O}_8^{2-}/\text{H}^{\oplus}$ | (2) $\text{PbO}_2/\text{H}^{\oplus}$ |
| (3) $\text{BiO}_3^{\ominus}/\text{H}^{\oplus}$ | (4) $\text{H}_2\text{O}_2/\text{H}^{\oplus}$ |

31. Select the correct statements

- (1) When CO_2 is passed into aqueous solution of CrO_4^{2-} , CrO_5 is formed
- (2) When CO_2 is passed into MnO_4^{2-} (green) solution it turns purple and a brown precipitate of MnO_2 is formed.
- (3) The yellow colour of CrO_4^{2-} is due to $d-d$ transition
- (4) The yellow colour of CrO_4^{2-} is due to charge transfer.

32. Select the correct statements:

- (1) MnO_2 dissolves in conc. HCl but does not form Mn^{4+} ion
- (2) MnO_4^{2-} is strongly oxidizing and stable only in very strong alkali.
- (3) KMnO_4 does not act as oxidizing agent in basic medium
- (4) Decomposition of acidic KMnO_4 is not catalysed by sunlight.

f-block**33. Select the correct statements:**

- (1) Sm^{2+} , Eu^{2+} and Yb^{2+} are good oxidizing agent.
- (2) Zr and Hf shows similar properties
- (3) $\text{La}(\text{OH})_3$ is the strongest base than the other lanthanum hydroxides.
- (4) Magnetic susceptibility values of actinides are greater than lanthanides.

34. Select the correct statements:

- (1) Ce^{3+} can be easily oxidized to Ce^{4+}
- (2) Chemical properties of all the lanthanoids are quite similar.
- (3) Gd^{3+} and Lu^{3+} are stable.
- (4) La^{4+} exists.

Miscellaneous Compounds**35. Which of the following statements are correct with reference to the ferrous and ferric ions?**

- (1) Fe^{3+} gives brown colour with potassium ferricyanide.
- (2) Fe^{2+} gives blue precipitate with potassium ferricyanide.
- (3) Fe^{3+} gives red colour with potassium thiocyanate.
- (4) Fe^{2+} gives brown colour with ammonium thiocyanate.

36. The aqueous solution of the salt will be coloured in the case of

- | | |
|--------------------------------|---------------------|
| (1) $\text{Zn}(\text{CO}_3)_2$ | (2) LiNO_3 |
| (3) $\text{Co}(\text{NO}_3)_2$ | (4) CrCl_3 |

7. In $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$, Fe has +2 state. It cannot be decided by
 (1) Magnetic measurement (2) Colligative property
 (3) Colour (4) Hybridisation

8. Which one of the following statements is/are correct?

- (1) Zinc dissolves in sodium hydroxide solution.
- (2) Carbon monoxide reduces iron(III) oxide to iron.
- (3) Mercury(II) iodide dissolves in excess of potassium iodide solution.
- (4) Tin(IV) chloride is made by dissolving tin solution in concentrated hydrochloric acid.

9. Select the correct statements

- (1) ZnCO_3 and CuO give metal on heating.
- (2) When CN^- ion is added to CuSO_4 , CN^- ion acts as oxidizing agent.
- (3) AgF is soluble in H_2O
- (4) Silver halides dissolve in thiosulphate and cyanide solution.

10. The species that undergo disproportionation in basic medium are:

- | | |
|----------------------|-------------------------|
| (1) ClO_4^- | (2) MnO_4^{2-} |
| (3) Cl_2 | (4) NO_2 |

Linked Comprehension Type

Paragraph 1

The colours of the transition metal are due to $d-d$ excitation. The energy required for $d-d$ electron excitation is available in the visible range.

Transition metal ions have the tendency to absorb certain radiations from the visible region and exhibit the complementary colour.

The transition metal ions which have completely filled d -orbitals are colourless as the excitation of electron or electrons is not possible within d -orbitals. The transition metal ions which have completely empty d -orbitals are also colourless. In KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, there are no unpaired electrons at the central atom and they are deep in colour. The colour of these compounds is due to charge transfer spectrum. For example, in MnO_4^- electron is momentarily transferred from O to the metal and thus oxygen changes from O^{2-} and O^- manganese from Mn^{7+} to Mn^{6+} .

1. Which of the following is paramagnetic as well as coloured ion?

- | | |
|----------------------|----------------------|
| (1) Cu^+ | (2) Cu^{2+} |
| (3) Sc^{3+} | (4) Zn^{2+} |

2. Which is a coloured ion?

- | | |
|----------------------------------------------|----------------------------------------------|
| (1) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ | (2) $[\text{Cu}(\text{CN})_4]^{3-}$ |
| (3) $[\text{Ti}(\text{H}_2\text{O})_6]^{4+}$ | (4) $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ |

3. Select the correct statement:

- (1) Colour of the transition metal ion arises due to $d-d$ transition.
- (2) Colour of certain oxysalts of transition metals is due to charge transfer.
- (3) Both are correct.
- (4) None is correct

4. Which of the following compounds is(are) coloured due to charge transfer spectra and not due to $d-d$ transitions?

- | | |
|---------------------|------------------------------|
| (1) KMnO_4 | (2) K_2CrO_4 |
| (3) CrO_3 | (4) All of these |

5. $\text{K}_2\text{Cr}_2\text{O}_7$ gives coloured solution in water. The colour is due to

- (1) $d-d$ transition in Cr-atoms
- (2) Presence of unpaired electron in d -orbital of oxygen
- (3) Charge transfer from O to Cr
- (4) None of the above

Paragraph 2

KMnO_4 is prepared from the mineral pyrolusite, MnO_2 (deep purple colour). It acts as an oxidising agent in the neutral, alkaline as well as acidic medium. In acidic medium, it is used in volumetric analysis for estimation of Fe^{2+} , $\text{Cr}_2\text{O}_4^{2-}$ salts etc.

The titrations are carried out in presence of H_2SO_4 . However, before using it as a titrant, it is first standardised with standard oxalic acid solution or Mohr's salt solution. In one of the experiments on titration 26.8 g of dry pure sodium oxalate ($\text{Mw} = 134 \text{ g mol}^{-1}$) was dissolved in 1L of distilled water and then 100 mL of 2M H_2SO_4 were added. The solution was cooled. Now to this solution, 0.1M KMnO_4 solution was added till a very faint pink colour persisted.

6. The purple colour of KMnO_4 is due to

- (1) Incomplete d -subshell
- (2) Ionic nature of KMnO_4
- (3) Charge transfer
- (4) Resonance in MnO_4^- ion

7. Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, is preferred over $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ for standardisation of KMnO_4 solution because

- (1) Mohr's salt is a double salt while ferrous sulphate is a single salt.
- (2) Mohr's salt is not hygroscopic but $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is hygroscopic.
- (3) Mohr's salt contains only ferrous ions whereas ferrous sulphate contains some ferric ions.
- (4) Mohr's salt solution can be titrated even in the absence of H_2SO_4 .

8. When pyrolusite is fused with KOH and KClO_3 , we get

- | | |
|-------------------------------------------------------|------------------------------|
| (1) KMnO_4 | (2) K_2MnO_4 |
| (3) Both KMnO_4 and K_2MnO_4 | (4) None of these |

9. If 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution were used in place of 0.1 M KMnO_4 in presence of H_2SO_4 in each case, the volume of 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution used would be

- | | |
|--------------|--------------|
| (1) 200 mL | (2) 400 mL |
| (3) 333.3 mL | (4) 666.6 mL |

10. If instead of H_2SO_4 , HCl or HNO_3 of suitable concentration were used, the volume of KMnO_4 solution used would have been

- (1) Less in case of HCl but more in case of HNO_3
- (2) More in case of HCl but less in case of HNO_3
- (3) More in both cases
- (4) Less in both cases

11. The volume of KMnO_4 solution that must have been added to obtain the faint pink colour at the end point must be
- (1) 100 mL (2) 200 mL
(3) 400 mL (4) 800 mL

Paragraph 3

Transition metals and many of their compounds show paramagnetic behaviour where there are unpaired electron or electrons. The magnetic moment arises from the spin and orbital motions in ions or molecule. Magnetic moment of n unpaired electrons is given as

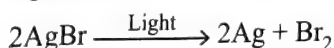
$$\mu = \sqrt{n(n+2)} \text{ Bohr Magnetron}$$

Magnetic moment increases as the number of unpaired electrons increases.

12. Which among the following ions has maximum value of magnetic moment
- (1) Cu^{2+} (2) Mn^{2+}
(3) Cr^{2+} (4) Ti^{2+}
13. Increasing value of magnetic moments of
(I) $[\text{Fe}(\text{CN})_6]^{4-}$ (II) $[\text{Fe}(\text{CN})_6]^{3-}$, (III) $[\text{Cr}(\text{NH}_3)_6]^{3+}$,
(IV) $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$ is:
- (1) $\text{I} < \text{II} < \text{III} < \text{IV}$ (2) $\text{IV} < \text{III} < \text{II} < \text{I}$
(3) $\text{II} < \text{III} < \text{I} < \text{IV}$ (4) $\text{I} < \text{II} < \text{IV} < \text{III}$
14. In 3d series the maximum magnetic moment is shown by
- (1) Sc (2) V
(3) Cr (4) Fe
15. Magnetic moments of Cr ($Z = 24$), Mn^\oplus ($Z = 25$) and Fe^{2+} ($Z = 26$) are x , y and z respectively. Which of the following order is correct?
- (1) $x < y < z$ (2) $x = y < z$
(3) $z < x = y$ (4) $x = y = z$
16. There are three unpaired electrons in $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and calculated value of magnetic moment on the basis of $\sqrt{n(n+2)}$ formula is 3.87 BM which is lower than the experimental value of 4.40 BM. The reason for this difference is due to
- (1) Increase in number of unpaired electrons during determination
(2) Some contribution of the orbital motion of the electrons to the magnetic moment
(3) $d-d$ transition
(4) Experimental error
17. Magnetic moment of $[\text{Ni}(\text{CN})_4]^{2-}$ is zero but that of $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$ is 2.83 BM. It is because of:
- (1) CN^\ominus is a strong ligand making two unpaired electrons in Ni^{2+} to pair up, while in $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$ two electrons remain unpaired as H_2O is a weak ligand
(2) Different oxidation state of Ni in two complexes
(3) Both (a) and (b)
(4) None of the above

Paragraph 4

Photography is based on the nature of silver halides. Except AgF, the silver halides are photosensitive. These undergo decomposition in light and turn black due to formation of free silver.



The photography films are prepared by adding 20% aqueous solution of AgNO_3 to NH_4Br solution containing gelatin. When such a film is exposed, emulsion gets affected and a latent image is formed on the film

When this exposed film or plate is dipped in a developer which contains a reducing agent, the parts affected most during exposure are reduced to the maximum. The image becomes visible. It is called a negative. The remaining sensitive emulsion on the negative is removed by dissolving it in hypo solution (fixer). Finally, a positive of the negative already prepared is made on silver bromide paper.

18. The compound formed on the unexposed photographic film or plate is
- (1) Silver nitrate (2) Ammonium bromide
(3) Diammine silver bromide (4) Silver bromide
19. The exposed part of the film or plate after developing contains
- (1) Silver metal (2) Silver oxide
(3) Silver bromide (4) Silver nitrate
20. Silver halides are used in photography because these compounds
- (1) Are insoluble in water
(2) Are affected by light
(3) Are soluble in ammonia solution
(4) Easily stick on the surface of photographic plate or film
21. The solution of the developer consists of
- (1) Alkaline solution of pyrogallol
(2) Alkaline solution of quinol
(3) Either (a) or (b)
(4) Neither (a) nor (b)
22. Silver bromide dissolves in hypo solution forming:
- (1) $\text{Ag}_2\text{S}_2\text{O}_3$ (2) Ag_2S
(3) $\text{Na}_3[\text{Ag}(\text{SO}_3)_2]$ (4) NaAgS_2O_3

Paragraph 5

In any transition series, from left to right, the d -orbitals are progressively filled and their properties vary accordingly.

23. In the second transition series, the largest number of oxidation states are shown by
- (1) Tc (2) Ru
(3) Rh (4) Pd
24. Which element do you expect to have the smallest atomic radius?
- (1) La (2) Zn
(3) Sc (4) Hg
25. Which element do you expect to have the highest melting point?
- (1) La (2) W
(3) Pt (4) Os
26. Which of the following pair of compounds is expected to exhibit same colour in aqueous solution?
- (1) FeCl_2 , CuCl_2 (2) VOCl_2 , CuCl_2
(3) VOCl_2 , FeCl_2 (4) FeCl_2 , MnCl_2

17. Which of the following is the correct order of second ionisation energy?

- (1) $V > Cr > Mn$
(3) $V < Cr > Mn$

(2) $V < Cr < Mn$

(4) $V > Cr < Mn$

Paragraph 6

18. $KMnO_4$ reacts with $Na_2S_2O_3$ in acidic, strongly basic and aqueous (neutral) media. 100 mL of $KMnO_4$ reacts with 100 mL of 0.1 M $Na_2S_2O_3$ in acidic, basic and neutral media.

19. The molarity (M) of $KMnO_4$ solution in the acidic medium

- (1) 0.2 M
(3) 0.4 M

(2) 0.02 M

(4) 0.04 M

20. The molarity (M) of $KMnO_4$ solution in basic medium is:

- (1) 0.8 M
(3) 0.26 M

(2) 0.08 M

(4) 0.026 M

21. The molarity (M) of $KMnO_4$ in aqueous medium is

- (1) 0.8 M
(3) 0.26 M

(2) 0.08 M

(4) 0.026 M

22. The molality (m) of $KMnO_4$ in the acidic medium is

(Density of $KMnO_4$ solution = 1.58 g mL^{-1} $M_w(KMnO_4)$

= 158 g mol^{-1})

(1) 0.025

(2) 0.25

(3) 0.12

(4) 0.012

Matrix Match Type

23. This section contains questions each with two columns—I and II.

24. Match the items given in column I with that in column II.

1. Match the column.

Column I (Metal ion)		Column II (Magnetic moment) ($(2M)$)	
a.	Cr^{3+}	p.	$\sqrt{35}$
b.	Fe^{2+}	q.	$\sqrt{30}$
c.	Ni^{2+}	r.	$\sqrt{24}$
d.	Mn^{2+}	s.	$\sqrt{15}$
		t.	$\sqrt{8}$

2. Match the column.

Column I		Column II	
a.	Ni	p.	Elements having same number of unpaired electron in their dipositive in column I
b.	Na	q.	At least 13 electrons are having magnetic quantum number 'zero'
c.	Mn	r.	Atom is paramagnetic
d.	Pd	s.	Element is not transition element
		t.	Element having pseudo inert gas configuration in its dipositive cation

3. Match the column.

Column I (Property)		Column II (Transition elements)	
a.	Highest oxidation state	p.	Cr
b.	Highest density	q.	Os
c.	Element with maximum unpaired electrons	r.	Tc
d.	Radioactive transition element	s.	Ru

4. Match the column.

Column I		Column II	
a.	K_2MnO_4	p.	Transition element in +6 oxidation state
b.	$KMnO_4$	q.	Paramagnetic
c.	$K_2Cr_2O_7$	r.	Manufactured from pyrolusite ore
d.	K_2CrO_4	s.	Manufactured from chromite ore

5. Match the column.

Column I (Alloys)		Column II (Constituents)	
a.	Gun metal	p.	Pb + Sn
b.	German silver	q.	Cu + Sb + Zn
c.	Brass	r.	Cu + Zn
d.	Solder	s.	Cu + Zn + Ni

6. Match the column.

Column I		Column II	
a.	Bayer's reagent	p.	$CuSO_4 + Ca(OH)_2$
b.	Bordeaux mixture	q.	1% alkaline $KMnO_4$
c.	Nessler's reagent	r.	Detection of unsaturation in organic compounds

7. Match the column.

Column I		Column II	
a.	Corrosive sublimate	p.	A white pigment
b.	Calomel	q.	$HgCl_2$
c.	Lithopone	r.	$ZnSO_4 \cdot 5H_2O$
d.	ZnO	s.	$BaSO_4 + ZnS$
e.	White vitriol	t.	Hg_2Cl_2

8. Match the column.

Column I		Column II	
a.	Rinmann's green	p.	Red form of HgS
b.	Pharash's serpent	q.	AgNO ₃
c.	Lunar caustic	r.	Cobalt zincate
d.	Vermilion	s.	Hg(CNS) ₂
e.	Verdigris	t.	Basic copper acetate

9. Match the column.

Column I		Column II	
a.	Tenorite	p.	Mixture of copper sulphide and FeS
b.	Parke's process	q.	Black oxide of Cu
c.	Deacon's process	r.	Silver
d.	Matte	s.	Impure copper
e.	Blister copper	t.	Cupric chloride

10. Match the items given in Column I with that in Column II and III.

Column I		Column II		Column III	
Compound		Characteristics (I)		Characteristics (II)	
a.	KMnO ₄	i.	$\text{KMnO}_4 \xrightarrow{\Delta} \dots\dots\dots + \text{MnO}_2 + \text{O}_2$ Blackish brown	p.	Dark green
b.	K ₂ MnO ₄	ii.	Prepared from pyrolusite ore.	q.	Oxidising agent in acidic medium
c.	K ₂ Cr ₂ O ₇	iii.	It oxidises I [⊖] to IO ₃ [⊖] in basic medium	r.	Orange red colour changes to yellow in basic medium
d.	K ₂ CrO ₄	iv.	Prepared from chromite ore.	s.	Yellow colour changes to orange red in acidic medium

11. Match the items given in Column I with that in Column II and III.

Column I		Column II		Column III	
Compound		Characteristics (I)		Characteristics (II)	
a.	Calomel	i.	HgCl ₂	p.	Ionic and gives 3 ions in aqueous solution
b.	Corrosive sublimate	ii.	It turns black with NH ₃	q.	Test for NH ₄ [⊕] ions
c.	Nessler's reagent	iii.	Hg ₂ Cl ₂	r.	Used in making ink.
d.	Lunar caustic	iv.	Alkaline solution of K ₂ [HgI ₄]	s.	Covalent and poisonous. Its antidote is white of an egg
		v.	AgNO ₃		

Numerical Value Type

- What is the value of x in the following equation.

$$\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^{\oplus} + x\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{Cr}^{3+} + 3\text{SO}_4^{2-} + 3\text{S} + 4\text{H}_2\text{O}$$
- What is the oxidation states of Cr in butterfly structure.
- What is the value of x in the following equation:

$$2\text{MnO}_4^{\ominus} + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \longrightarrow x\text{MnO}_2 + 4\text{H}^{\oplus}$$
- Out of the following, how many oxides are acidic.
 MnO, Mn₂O₃, MnO₂, MnO₃, Mn₂O₇
- Out of the following, how many of them have magnetic moment value $\sqrt{24}$ BM.
 Ti²⁺, Ti³⁺, V²⁺, Cr²⁺, Cr³⁺, Mn²⁺, Fe²⁺
- Out of the following how many of them are coloured compounds:
 MnO₄[⊖], Cr₂O₇²⁻, CrO₄²⁻, Sc³⁺, Ti⁴⁺, Zn²⁺, Mn³⁺, Cu²⁺, Fe²⁺, Fe³⁺
- Out of the following how many oxides are basic.
 TiO, Sc₂O₃, Ti₂O₃, VO, V₂O₅, CrO₃, Cr₂O₃, CuO, TiO₂
- What is the value of x in the Wilkinson's catalyst [RhCl(Ph₃P) _{x}] which is used as a homogenous catalyst in the hydrogenation of alkene.
- How many of the transition elements are called coinage metals?
- How many of the transition elements are called platinum metals?

Single Correct Answer Type

1. Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect?

- (1) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character
- (2) The ionic sizes of Ln (III) decrease in general with increasing atomic number
- (3) Ln (III) compounds are generally colorless
- (4) Ln (III) hydroxides are mainly basic in character

(AIEEE 2009)

2. In context with the transition elements, which of the following statements is incorrect?

- (1) In addition to the normal oxidation state, the zero oxidation state is also shown by these elements in complexes.
- (2) In the highest oxidation states, the transition metal shows basic character and forms cationic complexes
- (3) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding
- (4) Once the d^5 configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.

(AIEEE 2009)

3. The correct order of $E^\circ_{M^{3+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe, and Co is

- (a) $Mn > Cr > Fe > Co$
- (b) $Cr > Fe > Mn > Co$
- (c) $Fe > Mn > Cr > Co$
- (d) $Cr > Mn > Fe > Co$

(AIEEE 2010)

4. In context of the lanthanoids, which of the following statements is not correct?

- (1) There is a gradual decrease in the radii of the members with increasing atomic number in the series.
- (2) All the members exhibit +3 oxidation state.
- (3) Because of similar properties the separation of lanthanoids is not easy.
- (4) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.

(AIEEE 2011)

5. The outer electron configuration of Gd (At. no. 64) is

- (1) $4f^3, 5d^5, 6s^2$
- (2) $4f^8, d^0, 6s^2$
- (3) $4f^4, 5d^4, 6s^2$
- (4) $4f^7, 5d^1, 6s^2$

(AIEEE 2011)

6. Which of the following arrangements does not represent the correct order of the property stated against it?

- (1) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behavior
- (2) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
- (3) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution

(4) $Sc < Ti < Cr < Mn$: number of oxidation states

(JEE Main 2013)

7. The colour of $KMnO_4$ is due to

- (1) $M \rightarrow L$ charge transfer transition
- (2) d – d transition
- (3) $L \rightarrow M$ charge transfer transition
- (4) $\sigma - \sigma^*$ transition

(JEE Main 2015)

JEE ADVANCED

Single Correct Answer Type

1. The colour of light absorbed by an aqueous solution of $CuSO_4$ is

- (1) Orange red
- (2) Blue green
- (3) Yellow
- (4) Violet (IIT-JEE 2012)

2. In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agent respectively are

- (1) O_2 and CO_2
- (2) O_2 and Zn dust
- (3) HNO_3 and CO
- (4) HNO_3 and Zn dust

(IIT-JEE 2012)

3. Four successive members of first row transition element are listed below. Which one of them is expected to have highest $E^\circ_{M^{3+}/M^{2+}}$ value?

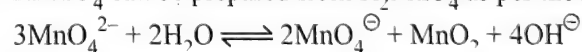
- (1) Mn (Z = 25)
- (2) Fe (Z = 26)
- (3) Co (Z = 27)
- (4) Cr (Z = 24)

(JEE Advanced 2013)

4. Which of the following statements about the interstitial compounds is incorrect?

- (1) They are much harder than the pure metal.
- (2) They have higher melting points than the pure metal.
- (3) They retain metallic conductivity.
- (4) They are chemically reactive. (JEE Advanced 2013)

5. $KMnO_4$ can be prepared from K_2MnO_4 as per the reaction:



The reaction can go to completion by removing OH^- ions by adding

- (1) CO_2
- (2) SO_2
- (3) HCl
- (4) KOH

(JEE Advanced 2013)

6. A magnetic moment of 1.73 B.M. will be shown by one among the following:

- (1) $TiCl_4$
- (2) $[CoCl_6]^{4-}$
- (3) $[Cu(NH_3)_4]^{2+}$
- (4) $[Ni(CN)_4]^{2-}$

(JEE Advanced 2013)

7. Which of the following lanthanoid ions is diamagnetic?

- (1) Eu²⁺
- (2) Yb²⁺
- (3) Ce²⁺
- (4) Sm²⁺

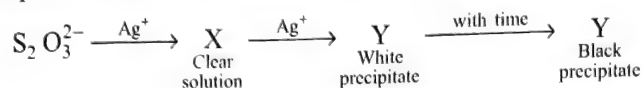
(JEE Advanced 2013)

8. The color of KMnO_4 is due to:

- (1) $M \rightarrow L$ charge transfer transition
- (2) $d-d$ transition
- (3) $L \rightarrow M$ charge transfer transition
- (4) $\sigma-\sigma^*$ transition

(JEE Advanced 2015)

9. In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively, are



- (1) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$, $\text{Ag}_2\text{S}_2\text{O}_3$, Ag_2S
- (2) $[\text{Ag}(\text{S}_2\text{O}_3)_3]^{5-}$, Ag_2SO_3 , Ag_2S
- (3) $[\text{Ag}(\text{SO}_3)_2]^{3-}$, $\text{Ag}_2\text{S}_2\text{O}_3$, Ag
- (4) $[\text{Ag}(\text{SO}_3)_3]^{3-}$, Ag_2SO_4 , AgS

(JEE Advanced 2016)

10. Which of the following combination will produce H_2 gas?

- (1) Fe metal and conc. HNO_3
- (2) Cu metal and conc. HNO_3
- (3) Zn metal and $\text{NaOH}(\text{aq})$
- (4) Au metal and $\text{NaCN}(\text{aq})$ in the presence of air

(JEE Advanced 2017)

Multiple Correct Answers Type

1. Reduction of the metal centre in aqueous permanganate ion involves

- (1) 3 electrons in neutral medium
- (2) 5 electrons in neutral medium
- (3) 3 electrons in alkaline medium
- (4) 5 electrons in acidic medium

(IIT-JEE 2011)

2. The equilibrium $2\text{CuI} \rightleftharpoons \text{Cu} + \text{Cu}^{\text{II}}$

in aqueous medium at 25°C shifts towards the left in the presence of

- (1) NO^\ominus
- (2) Cl^\ominus
- (3) SCN^\ominus
- (4) CN^\ominus

(IIT-JEE 2011)

3. Which one of the following arrangements does not represent the correct order of the property stated against it?

- (1) $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$: ionic size
- (2) $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$: stability in aqueous solution
- (3) $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$: number of oxidation states
- (4) $\text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$: paramagnetic behaviour

(JEE Advanced 2013)

4. The correct statement(s) about Cr^{2+} and Mn^{3+} is (are)

[Atomic numbers of Cr = 24 and Mn = 25]

- (1) Cr^{2+} is a reducing agent
- (2) Mn^{3+} is an oxidizing agent
- (3) Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration
- (4) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration

(JEE Advanced 2015)

5. Fe^{3+} is reduced to Fe^{2+} by using

- (1) H_2O_2 in presence of NaOH
- (2) Na_2O_2 in water

- (3) H_2O_2 in presence of H_2SO_4
- (4) Na_2O_2 in presence of H_2SO_4

(JEE Advanced 2015)

6. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are) (Atomic number: Fe = 26, Ni = 28)

- (1) Total number of valence shell electrons at metal centre in $\text{Fe}(\text{CO})_5$ or $\text{Ni}(\text{CO})_4$ is 16
- (2) These are predominantly low spin in nature
- (3) Metal-carbon bond strengthens when the oxidation state of the metal is lowered
- (4) The carbonyl C-O bond weakens when the oxidation state of the metal is increased

(JEE Advanced 2018)

Linked Comprehension Type

Paragraph 1

p-Amino-*N,N*-dimethylaniline is added to a strongly acidic solution of X. The resulting solution is treated with a few drops of aqueous solution of Y to yield blue colouration due to the formation of methylene blue. Treatment of aqueous solution of Y with reagent potassium hexacyanoferrate (II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, the treatment of the solution of Y with the solution of potassium hexacyanoferrate (III) leads to a brown colouration due to the formation of Z.

1. Compound X is

- (1) NaNO_3
- (2) NaCl
- (3) Na_2SO_4
- (4) Na_2S

2. Compound Y is

- (1) MgCl_2
- (2) FeCl_2
- (3) FeCl_3
- (4) ZnCl_2

3. Compound Z is

- (1) $\text{Mg}_2[\text{Fe}(\text{CN})_6]$
- (2) $\text{Fe}[\text{Fe}(\text{CN})_6]$
- (3) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
- (4) $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$

(IIT-JEE 2009)

Paragraph 2

Copper is the most noble of the first row transition elements. It occurs in small deposits in several countries. Ores of copper include chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), atacamite [$\text{Cu}_2\text{Cl}(\text{OH})_3$], cuprite (Cu_2O), copper glance (Cu_2S), and malachite [$\text{Cu}_2(\text{OH})_2\text{CO}_3$]. However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS_2). Extraction of copper from chalcopyrite includes roasting, iron removal; and self-reduction.

4. Partial roasting of chalcopyrite produces

- (1) Cu_2S and FeO
- (2) Cu_2O and FeO
- (3) CuS and Fe_2O_3
- (4) Cu_2O and Fe_2O_3

5. Iron is removed from chalcopyrite as

- (1) FeO
- (2) FeS
- (3) Fe_2O_3
- (4) FeSiO_3

6. In self-reduction, the reducing species is

- (1) S
- (2) O^{2-}
- (3) S^{2-}
- (4) SO_2

(IIT-JEE 2010)

Paragraph 3

When a metal rod M is dipped into an aqueous colourless concentrated solution of compound N, the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate O. Addition of aqueous NH_3 dissolves O and gives an intense blue solution.

7. The metal rod M is

- (1) Fe (2) Cu
(3) Ni (4) Co

8. The compound N is

- (1) AgNO_3 (2) $\text{Zn}(\text{NO}_3)_2$
(3) $\text{Al}(\text{NO}_3)_3$ (4) $\text{Pb}(\text{NO}_3)_2$

9. The final solution contains

- (1) $[\text{Pb}(\text{NH}_3)_4]^{2+}$ and $[\text{CoCl}_4]^{2-}$
(2) $[\text{Al}(\text{NH}_3)_4]^{3+}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$
(3) $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$
(4) $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$

(IIT-JEE 2011)

Matrix Match Type

1. Match the column.

Column I Nature of reaction/type		Column II Products	
a.	$\text{O}_2^- \longrightarrow \text{O}_2 + \text{O}_2^{2-}$	p.	Redox reaction
b.	$\text{CrO}_4^{2-} + \text{H}^+ \longrightarrow$	q.	One of the products has trigonal planar structure
c.	$\text{MnO}^+ + \text{NO}_2^- + \text{H}^+ \longrightarrow$	r.	Dimeric bridged tetrahedral metal ion
d.	$\text{NO}_3^- + \text{H}_2\text{SO}_4 + \text{Fe}^{2+} \longrightarrow$	s.	Disproportionation

(IIT-JEE 2007)

2. Match each of the reactions given in column I with the corresponding product(s) given in column II.

Column I		Column II	
a.	$\text{Cu} + \text{dil HNO}_3$	p.	NO
b.	$\text{Cu} + \text{conc HNO}_3$	q.	NO_2
c.	$\text{Zn} + \text{dil HNO}_3$	r.	N_2O
d.	$\text{Zn} + \text{conc HNO}_3$	s.	$\text{Cu}(\text{NO}_3)_2$
		t.	$\text{Zn}(\text{NO}_3)_2$

(IIT-JEE 2009)

Numerical Value Type

1. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is

(IIT-JEE 2009)

2. The number of water molecule(s) directly bonded to the metal centre in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is

(IIT-JEE 2009)

3. Among the species given below, the total number of diamagnetic species is _____.

H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapour phase,

Mn_3O_4 , $(\text{NH}_4)_2[\text{FeCl}_4]$, $(\text{NH}_4)_2[\text{NiCl}_4]$, K_2MnO_4 , K_2CrO_4

(JEE Advanced 2018)

4. To measure the quantity of MnCl_2 dissolved in an aqueous solution, it was completely to KMnO_4 using the reaction. $\text{MnCl}_2 + \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{KMnO}_4 + \text{HCl}$ (equation not balanced). Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 mg) was added in portions till the colour of the permanganate ion disappeared. The quantity of MnCl_2 (in mg) present in the initial solution is _____.

(Atomic weights in g mol^{-1} : Mn = 55, Cl = 35.5)

(JEE Advanced 2018)

Answers Key

EXERCISES

Single Correct Answer Type

1. (3) 2. (2) 3. (3) 4. (2) 5. (1)
6. (4) 7. (1) 8. (4) 9. (2) 10. (1)
11. (4) 12. (3) 13. (2) 14. (4) 15. (2)
16. (1) 17. (2) 18. (4) 19. (2) 20. (2)
21. (4) 22. (2) 23. (3) 24. (1) 25. (4)
26. (1) 27. (2) 28. (4) 29. (1) 30. (2)
31. (3) 32. (3) 33. (3) 34. (1) 35. (1)
36. (1) 37. (1) 38. (1) 39. (4) 40. (2)
41. (3) 42. (1) 43. (4) 44. (2) 45. (3)

46. (1) 47. (2) 48. (3) 49. (4) 50. (2)
51. (1) 52. (1) 53. (1) 54. (4) 55. (4)
56. (3) 57. (2) 58. (1) 59. (4) 60. (4)
61. (3) 62. (3) 63. (3) 64. (3) 65. (1)
66. (1) 67. (3) 68. (2) 69. (4) 70. (3)
71. (3) 72. (1) 73. (4) 74. (2) 75. (1)
76. (2) 77. (1) 78. (2) 79. (2) 80. (2)
81. (1) 82. (2) 83. (1) 84. (4) 85. (4)
86. (2) 87. (2) 88. (4) 89. (3) 90. (4)
91. (1) 92. (4) 93. (3) 94. (2) 95. (2)
96. (4) 97. (1) 98. (3) 99. (4) 100. (2)

101. (4) 102. (3) 103. (2) 104. (4) 105. (3)
 106. (4) 107. (2) 108. (2) 109. (3) 110. (1)
 111. (1) 112. (1) 113. (2) 114. (3) 115. (3)
 116. (1) 117. (3) 118. (3) 119. (2) 120. (4)
 121. (4) 122. (4)

Multiple Correct Answers Type

1. (1, 2) 2. (3, 4) 3. (1, 2)
 4. (2, 3) 5. (1, 3, 4) 6. (1, 3, 4)
 7. (1, 4) 8. (1, 2, 4) 9. (1, 2)
 10. (2, 3, 4) 11. (2, 3) 12. (1, 3)
 13. (1, 2) 14. (1, 3, 4) 15. (2, 3)
 16. (1, 2, 3) 17. (1, 2, 4) 18. (1, 2, 3)
 19. (1, 2, 3) 20. (1, 3) 21. (1, 2, 3)
 22. (2, 3, 4) 23. (1, 2, 3) 24. (1, 2)
 25. (1, 2, 4) 26. (1, 2, 4) 27. (2, 3)
 28. (1, 3, 4) 29. (1, 2) 30. (1, 2, 3)
 31. (2, 3) 32. (1, 2) 33. (2, 3, 4)
 34. (1, 2, 3) 35. (1, 2, 3) 36. (3, 4)
 37. (2, 3, 4) 38. (1, 2, 3) 39. (3, 4)
 40. (2, 3, 4)

Linked Comprehension Type

1. (2) 2. (1) 3. (3) 4. (4) 5. (3)
 6. (3) 7. (3) 8. (2) 9. (4) 10. (2)
 11. (4) 12. (2) 13. (4) 14. (3) 15. (3)
 16. (2) 17. (1) 18. (4) 19. (1) 20. (2)
 21. (3) 22. (3) 23. (3) 24. (2) 25. (2)
 26. (2) 27. (3) 28. (2) 29. (1) 30. (3)
 31. (4)

Matrix Match Type

Q. No.	a	b	c	d	e
1.	s	r	t	p	—
2.	p, q, r	r, s	q, r	p, q	—
3.	q, s	q	p	r	—
4.	p, q, r	r	p, s	p, s	—
5.	q	s	r	p	—

6.	q, r	p	s	—
7.	q	t	s	p
8.	r	s	q	p
9.	q	r	t	p
10.	ii, iii → q	i, ii → p, q	iv → q, r	iv → s
11.	ii, iii → p	i → s	iv → q	v → r

Numerical Value Type

1. (3) 2. (6) 3. (5) 4. (3) 5. (2)
 6. (7) 7. (4) 8. (3) 9. (3) 10. (6)

ARCHIVES**JEE Main****Single Correct Answer Type**

1. (3) 2. (2) 3. (1) 4. (4) 5. (4)
 6. (1) 7. (3)

JEE Advanced**Single Correct Answer Type**

1. (1) 2. (2) 3. (3) 4. (4) 5. (1)
 6. (3) 7. (2) 8. (3) 9. (1) 10. (3)

Multiple Correct Answers Type

1. (1, 4) 2. (2, 3, 4) 3. (2, 4) 4. (1, 2, 3) 5. (1, 2)
 6. (2, 3)

Linked Comprehension Type

1. (4) 2. (3) 3. (2) 4. (1) 5. (4)
 6. (3) 7. (2) 8. (1) 9. (3)

Matrix Match Type

1. (a → p, s; b → r; c → p, q; d → p)
 2. (a → p, s; b → q, s; c → r, t; d → q, t)

Numerical Value Type

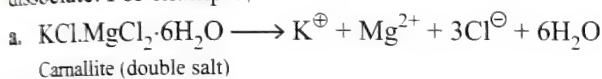
1. (6) 2. (4) 3. (1) 4. (126)

OVERVIEW

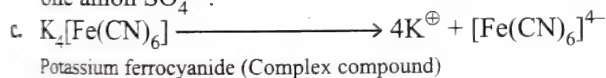
1. **Coordination compounds:** Compounds in which the central atom is linked to a number of ions or neutral molecules called ligands by coordinate bonds i.e., by donation of lone pair of electrons by ligands to the central metal atom are called coordination compounds.

2. **Double salts, mixed salts and complex compounds:** Both double salts and complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. Hence, they are additional molecular compounds.

However, double salts dissociate into simple substances or ions completely when dissolved in water, whereas in complex compounds, the complex ion almost does not dissociate. For example,



b. Bleaching powder CaOCl_2 is a mixed salt. It is a salt of Ca^{2+} in which the anions present are Cl^{\ominus} and ClO^{\ominus} (hypochlorite ion). Similarly, NaKSO_4 is a mixed salt in which there are two cations Na^{\oplus} and K^{\oplus} ions and one anion SO_4^{2-} .



3. **Ligands and central metal atom/ion:** The donor atoms, molecules or anions which donate a pair of electrons to the metal atom or ion and form a coordinate bond with it are called **ligands**. The metal atom or ion to which these ligands are attached is called **central metal atom or ion**.

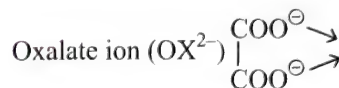
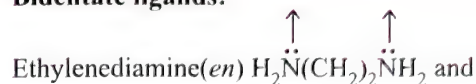
4. **Denticity:** The number of coordinating or ligating groups present in a ligands is called the **denticity of that ligand**.

5. **Types of ligands:** Ligands can be of the following types depending on the denticity of the ligand.

a. **Monodentate or unidentate ligand:** They have one donor atom, i.e. they donate only one lone pair of electrons to the central atom e.g., X^{\ominus} , $\text{H}_2\ddot{\text{O}}$, $\ddot{\text{N}}\text{H}_3$, CO , SCN^{\ominus} etc.

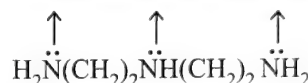
b. **Polydentate or multidentate ligands:** These ligands coordinate using two or more donor atoms. Name and structures of some of them are shown below:

i. **Bidentate ligands:**



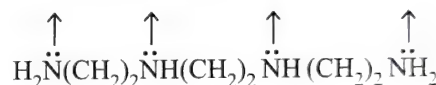
ii. **Tridentate or terdentate ligands:**

Diethylenetriamine (diene):



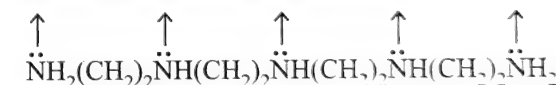
iii. **Tetradentate ligand:**

Triethylene tetraamine (triene):



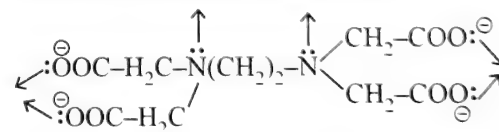
iv. **Pentadentate ligand:**

Tetraethylenepentaamine(tetraene):

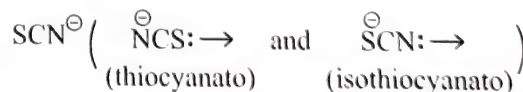
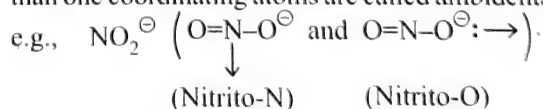


v. **Hexadentate ligand:**

Ethylene diaminetetraacetato ion:



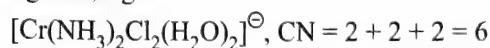
6. **Ambidentate ligands:** Unidentate ligands containing more than one coordinating atoms are called ambidentate ligands.



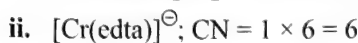
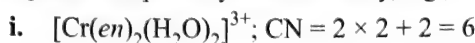
7. **Flexidentate ligands:** Ligands which have more than one donor site, like SO_4^{2-} , CO_3^{2-} etc. such ligands can behave as monodentate ligand in one complex and bidentate in another complexes are known as flexidentate ligands.

EDTA generally acts as a hexadentate ligand but it can also act as a pentadentate and tetradentate ligand.

8. Coordination number (CN): It is defined as the number of coordinate bonds formed with the central atom/ion by the ligands, e.g.



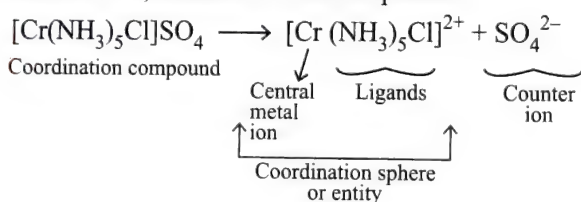
Coordination number in case of polydentate ligands attached to central metal atom/ion is equal to number of polydentate ligand multiplied by their denticity, e.g.,



9. Coordination number (CN) of some central metal atom/ion. (Refer to Table 7.6).

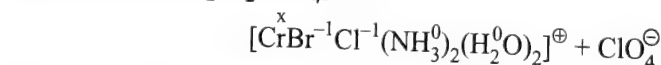
10. Coordination sphere or coordination entity and counter ion: The central atom and the ligands which are directly attached to it are enclosed in square brackets and are collectively termed as coordination sphere or coordination entity.

The ionisable groups outside the square brackets are called counter ions, as shown in the compounds.



11. Coordination polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central metal atom/ion in a definite direction thereby giving a definite geometry to the complex compound/ion is called coordination polyhedron around the central metal atom/ion. The various polyhedra are tetrahedral, square planar, octahedral, square pyramidal, trigonal bipyramidal, pentagonal bipyramidal etc.

12. Oxidation number (ON) of central atom: It is defined as the charge that central metal ion would carry if all the ligands are removed along with electron pairs. For example,



Charge on complex ion = +1

Let charge on Cr = x

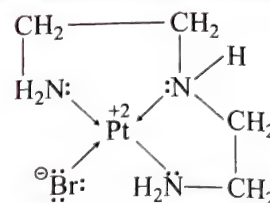
Total charge of ligands = -1 - 1 + 0 + 0 = -2

$\therefore x - 2 = +1 \therefore x = 3$

Hence oxidation number of Cr = +3 or (III).

Note: The central atom in a complex compound/ion can be even a non-metal, e.g., in $\text{Ba}[\text{BrF}_4]_2$, central atom in complex ion is Br.

13. Chelation: When coordination of two or more donor atoms from a polydentate ligand to a single central atom/ion takes place forming a closed or cyclic ring structure, it is called chelation and the ligand is called a chelating ligand. The close ring compound thus formed is called chelate (or metal chelate). [Chelos, Greek word means 'crab']. For example, Tridentate chelation in $[\text{PtBr}(\text{dien})]^\oplus$



Chelating ligands form more stable complexes than monodentate analogous.

14. Homoleptic, heteroleptic and labile complexes: Complex in which the metal atom/ion is linked to only one type of ligands are called **homoleptic complexes**, e.g., $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. The complexes in which the metal atom/ion is linked to more than one kind of ligands are called **heteroleptic complexes**, e.g., $[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Br}_2]^\oplus$. The complex in which ligand can easily be replaced by other ligands is called **labile complex**.

15. Homonuclear and polynuclear complexes: Complexes in which only one metal atom is present are known as homonuclear complexes, e.g., $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. Complexes in which more than one metal atom/ion is present are known as polynuclear complexes, e.g., $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2]$

16. Nomenclature and formula writing of coordination compounds: Refer to Section 7.5.

17. a. Werner's coordination theory: Refer to Section 7.6.

b. Werner's representation of complexes: For example in $\text{CoBr}_3 \cdot x\text{NH}_3$, the maximum value of $x = \text{CN of Co}^{3+}$ which is equal to 6.

The minimum value of $x = \text{CN} - \text{O.S.} = 3$

Werner's coordination compounds

	Werner complex and colour	Modern notation	Ionisation	Primary valency satisfied by (ON)	Secondary valency satisfied by CN
(A)	$\text{CoCl}_3 \cdot 6\text{NH}_3$ Yellow	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^\ominus$	3Cl^\ominus	6NH_3
(B)	$\text{CoCl}_3 \cdot 5\text{NH}_3$ Purple	$[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$	$[\text{CoCl}(\text{NH}_3)_5]^{2+} + 2\text{Cl}^\ominus$	3Cl^\ominus including one Cl^\ominus with both valencies)	5NH_3 one Cl^\ominus
(C)	$\text{CoCl}_3 \cdot 4\text{NH}_3$ Exists in 2 isomers <i>cis</i> & <i>trans</i> with green and violet in colour	$[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$	$[\text{CoCl}_2(\text{NH}_3)_4]^\oplus + \text{Cl}^\ominus$	3Cl^\ominus including 2Cl^\ominus with both valencies)	4NH_3 2Cl^\ominus
(D)	$\text{CoCl}_3 \cdot 3\text{NH}_3$	$[\text{CoCl}_3(\text{NH}_3)_3]$	$[\text{CoCl}_3(\text{NH}_3)_3]$	3Cl^\ominus all with both valencies or with dual	3NH_3 3Cl^\ominus

Note: Conductance of the above complex will be in the order of $A > B > C > D$.

c. **Failure of Werner's coordination theory:** Refer to Section 7.6.2.

18. Sidgwick theory and effective atomic number (EAN):

In order to explain the stability of complexes Sidgwick proposed EAN rule. He suggested that a metal ion will continue accepting electron pairs till the total number of electrons in the metal ion (after gaining one lone pair of electrons from the ligands) becomes equal to that of next higher noble gas. This total number of electrons is called EAN of the metal.

$$\text{EAN} = (\text{Atomic number} - \text{OS}) + (\text{CN} \times 2)$$

For example,

i. EAN in $[\text{Fe}^{2+}(\text{CN})_6]^{4-} = (26 - 2) + (6 \times 2) = 36$

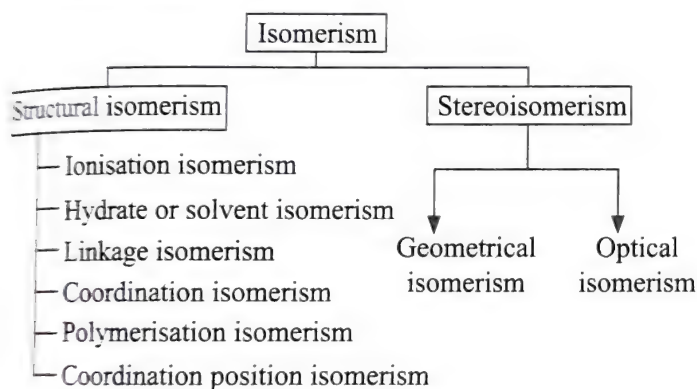
= Z of Kr (36) (next nearest inert gas).

ii. EAN in $[\text{Fe}^{3+}(\text{CN})_6]^{3-} = (26 - 3) + (6 \times 2) = 35$

≠ Z of Kr (36) (next nearest inert gas).

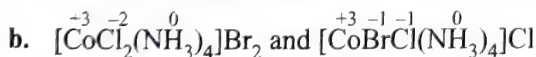
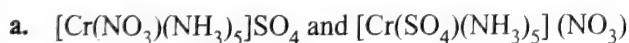
EAN rule is not valid in this case.

19. **Isomerism:** Isomers are compounds having same molecular formula but different structures. The following types of isomerism are:

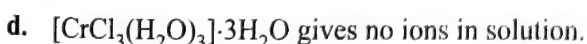
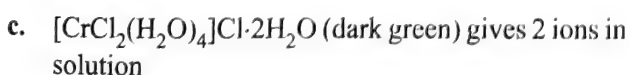
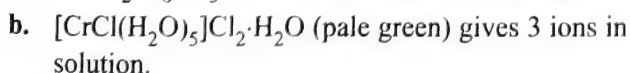


20. Structural isomerism:

i. **Ionisation isomerism:** This type of isomerism exists when a counter ion in a coordination compound is itself a potential ligand. For example,



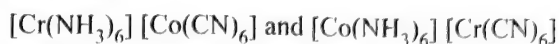
ii. **Hydrate or solvent isomerism:** It occurs when water forms a part of the coordination entity or is outside it. For example, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ exists in



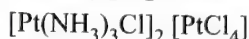
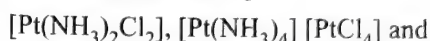
iii. **Linkage isomerism:** This type of isomerism is possible in any coordination compounds containing an ambidentate ligand like NO_2^- , or SCN^- or CN^- . This type of isomerism arises due to different metal-ligand (M ← L) linkage. For example, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$

has two isomeric forms having red and yellow colours. The red colour isomer is $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ (having Co ← O linkage) while the yellow isomer is $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ (having Co ← N linkage).

iv. **Coordination isomerism:** Coordination compounds made up of cationic and anionic coordination entities, show this type of isomerism due to interchange of ligands between the cation and anion entities. For example,

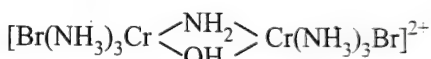
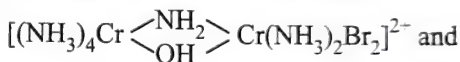


v. **Polymerisation isomerism:** This type of isomerism exists among complexes which have same empirical formula but each of the isomer is some multiple of the empirical formula, e.g.



These isomers are distinguished by mass spectroscopic methods.

vi. **Coordination position isomerism:** This type of isomerism is shown in polynuclear complexes due to interchange of ligands between the coordination spheres of various central metal ion, e.g.,



vii. **Stereoisomerism:** This type of isomerism is due to differences in arrangement of ligands in space around a given metal atom/ion. It is of the following two types:

A. Geometrical isomers (GI):

cis-trans isomerism: This type of isomerism occurs in complexes having coordination number (CN) 4 (square planar) and 6 (octahedral) complexes.

a. Complexes with general formula Ma_4 , Mab_3 and Ma_3b (square planar geometry with CN = 4) and Ma_6 and Ma_5b or Mab_5 (octahedral geometry with CN = 6) **do not show GI**.

b. Complexes with general formula Ma_2b_2 (where both 'a' and 'b' are monodentate) shows 2 isomers (*cis* and *trans*), e.g., $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

c. Ma_2bc type shows 2 isomers (*cis* and *trans*), e.g., $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]$

d. Mabcd type shows 3 geometrical isomers, e.g., $[\text{Pt}(\text{NH}_3)\text{ClBrI}]$

e. Square planar complexes having unsymmetrical bidentate ligands, show 2 GI (*cis* and *trans*) e.g., $[\text{Pt}(\text{Gly})_2]$.

f. Octahedral complexes of type Ma_4b_2 and Ma_3b_3 each exhibit 2 G.I. respectively. In case of Ma_4b_2 it is classified as *cis* and *trans* and in case of Ma_3b_3 , it is classified as facial (*fac*-) and meridional (*mer*-).

g. Octahedral complexes of type Mabcdef can have 15 geometrical isomers.

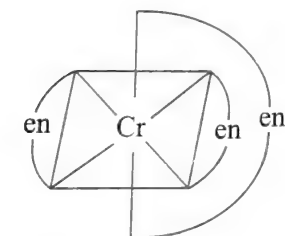
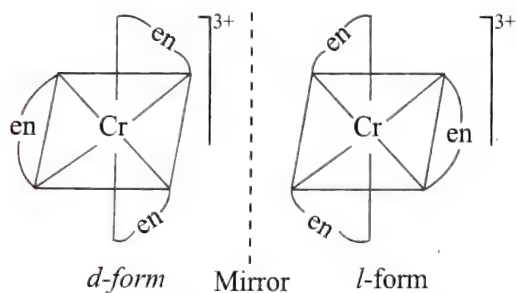
- h. Geometrical isomers do not occur in tetrahedral complexes (CN = 4) because the relative position of the ligands attached to the central metal atom/ion is same w.r.t. each other.

B. Optical isomerism:

- a. The coordination compounds having same molecular formula but differing in their ability to rotate directions of the plane of polarised light are said to exhibit optical isomerism and such molecules are called optical isomers (enantiomers or enantiomorphs).
- b. General formulae of optically active complexes
- $[M(AA)_3]^{n\pm}$, $[M(AA)_2a_2]^{n\pm}$, $[M(AA)_2ab]^{n\pm}$, $[M(AA)a_2b_2]^{n\pm}$,
(where AA are symmetrical bidentate ligands)
 - $[Ma_2b_2c_2]^{n\pm}$, $[Mabcdef]^{n\pm}$, $[M(AB)_3]^{n\pm}$
(where AB are unsymmetrical ligands)

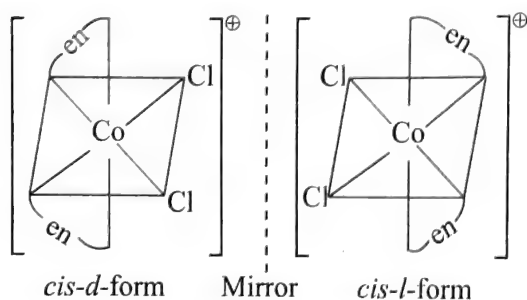
C. Some examples:

- i. $[M(AA)_3]^{n\pm}$, e.g., $[Cr(en)_3]^{3+}$ (3 stereoisomers)



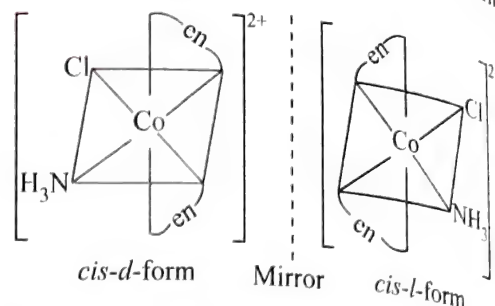
'Meso' or optically inactive form (if exists)

- ii. $[M(AA)_2a_2]^{n\pm}$, e.g., $[Co(en)_2Cl_2]^{\oplus}$
cis form = 3, (each showing optical isomerism)
trans form = 1 (does not show optical isomerism)

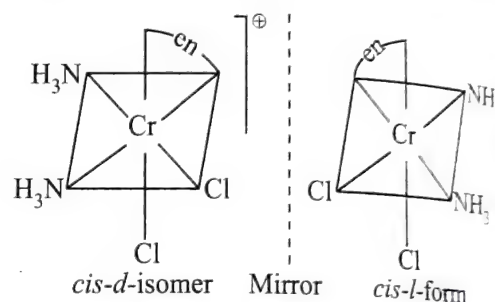


- iii. $[M(AA)_2ab]^{n\pm}$, e.g., $[Co(en)_2(NH_3)Cl]^{2+}$
 (3 stereoisomers)
 (one *cis* and one *trans*)

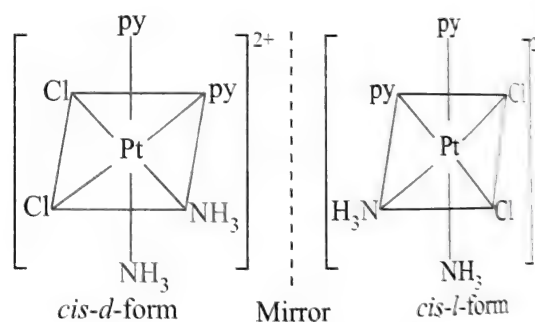
cis form is optically active but the *trans* form is optically inactive.



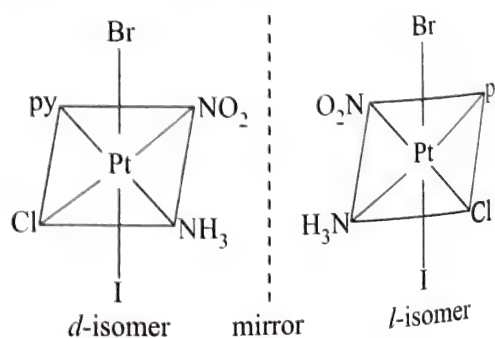
- iv. $[M(AA)a_2b_2]^{n\pm}$, e.g., $[CrCl_2(en)(NH_3)_2]^{\oplus}$
 (one *cis* and one *trans*)
cis form is optically active but *trans* form is optically inactive.



- v. $[Ma_2b_2c_2]^{n\pm}$, e.g., $[Pt(py)_2(NH_3)_2Cl_2]^{2-}$
 (one *cis* and one *trans*)
cis form is optically active but *trans* form is optically inactive.



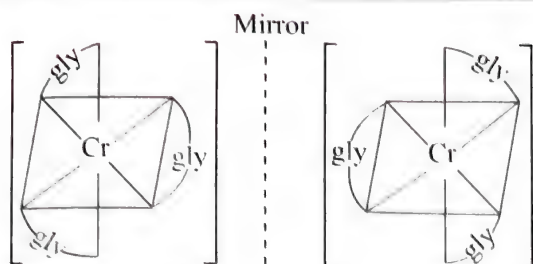
- vi. $[Mabcdef]^{n\pm}$, e.g., $[Pt(py)NH_3NO_2ClBrI]$ shows 15 geometrical isomers. Each of them is optically active. Only 3 isomers have been prepared but no form has been resolved.



- vii. $[M(AB)_3]$, e.g., $[Cr(gly)_3]$

2 *cis* and 2 *trans* forms.

Both the forms are optically active.



cis or trans-d-isomer

cis or trans-l-isomer

viii. Both $[Ma_4b_2]^{n+}$ and $[Ma_3b_3]^{n+}$ types show two geometrical isomers (*cis* and *trans*) or *fac*- and *mer*-. But none of them are optically active.

ix. Octahedral complexes containing hexadentate ligands e.g., $[Cr(edta)]^\ominus$ show optical isomerism, i.e., *d*- and *l*-form.

21. **Bonding in coordination compounds:** To explain the definite geometry, magnetic and optical properties of coordination compounds, various theories were put forward, e.g.,

- Valence bond theory (VBT) in 1930s
 - Crystal field theory (CFT) in 1950s and 1960s
 - Ligand field theory (LFT) in 1960s onwards
 - Molecular orbital theory (MOT) in 1960s onwards
- But only first two theories are discussed in this chapter.

22. a. **Valence bond theory (VBT):** Refer to Section 7.10

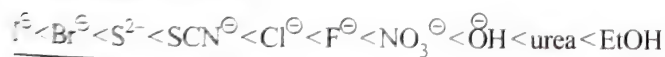
b. **Drawbacks of VBT:** (Refer to Section 7.10.6)

c. Refer to Table 7.17, for geometry (shape), hybridisation and magnetic properties of some of the complexes.

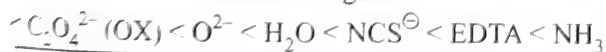
23. **Crystal field theory (CFT):** (Refer to Section 7.11)

24. **Spectrochemical Series:**

Some ligands have been arranged below from the weakest to the strongest. This arrangement is called spectrochemical series as shown below:



Weak field ligand



Border line field ligands



Strong field ligands

A pattern of increasing σ donation is:

Halide donors < N donors < C donors

Note: Oxalate, generally behaves as weak field ligand but with Co (cobalt), it behaves as a strong field ligand like NH_3 e.g., in the compound $[Co(OX)_3]^{3-}$.

25. **Limitation of CFT:**

- Assuming ligands as point charges, it follows that anionic ligands should exert greatest splitting effect, but anionic ligands are found at low end of the spectrochemical series.

- OH^\ominus lies below H_2O and NH_3 in spectrochemical series, but it produces a greater splitting.

These above weakness of CFT are explained by LFT (Ligand field theory)

26. **Stability of coordination compounds:** (Refer to Section 7.14)

27. **Organometallic compound (OMC):** They contain at least one M-C bond. $[Ni(CO)_4]$ is taken as OMC although CO is not organic compound. Metal cyanides (e.g. KCN) are not included in OMC, although they contain M-C bond.

A. **OMC are of two types:**

- s- and p-block OMC or σ complexes
- d- and f-block OMC or π -complexes.

s- and p-block OMC: The bonds in alkyls of s-block elements are highly polar.

In the OMC of group 14, 15 and 16, M-C bonds are of relative lower polarity.

Methyl compounds of Li, Na, Be, Mg and Al are associated with alkyl bridges and multicentre 2 electron bond. e.g., $Li_4(CH_3)_4$, $Al_2(CH_3)_6$.

B. d- and f-block O.M.C.

- Zeise's salt: $[PtCl_3(C_2H_4)]^\ominus$ or $K[PtCl_3(\eta^2-C_2H_4)]$
- $[Ni(CO)_4]$, $[Cr(CO)_6]$, $Co_2(CO)_8$, $[Fe_2(CO)_9]$, $[Mn_2(CO)_{10}]$, $Fe(CO)_5$, $Fe_3(CO)_{12}$.

iii. **Ferrocene:**

$[Fe(\eta^5-C_5H_5)_2]$ (bicyclopentadienyl iron(II)) and dibenzene chromium $[Cr(\eta^6-C_6H_6)_2]$

These compounds are called METALLOCENE or sandwich compounds which have π -bonding of carbocyclic rings to metal atoms.

They are highly specific for homogeneous catalysis process like carbonylation, hydrogenation and polymerisation.

28. a. **Metal carbonyls:** Homoleptic carbonyls (compounds containing CO ligands only) formed by most of TE.

Metal carbonyls are not regarded as organometallic compounds (OMC) in the true sense because CO is not an organic compound. However, they are studied along with other OMCs.

- Nature of bonding in metal carbonyls:** CO, as a ligand binds to CMA by C-atom forming weak σ -bond to the CMA, CO acts also as an acceptor ligand and forms a π -bond to the metal. This is called **synergic bonding** which stabilises the (M-L) interaction.

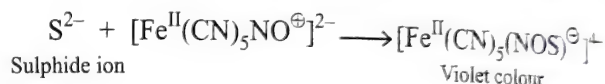
29. **Importance of coordination compounds:**

- cis*-platin and taxol are used in cancer (tumours) therapy.
- Coordination compounds are of great importance to biological system e.g.
 - Chlorophylls (the green plant pigment that acts as a photosensitiser in the photosynthesis in plants Ligand = Porphyrin, CMA = Mg^{2+})
 - Haemoglobin (acts as O_2 carrier, red pigment of blood) [Ligand = Porphyrin, CMA = Fe^{2+}]

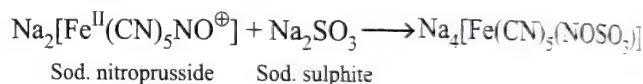
- iii. Myoglobin (which stores O_2 and is a regulator of respiration. (Ligand = Porphyrin, CMA = Fe^{2+})
- iv. Vitamin B_{12} or cyanocobalamine (antipernicious anaemia factor. Ligand = Corrin, CMA = Co^{2+})
- v. Enzyme e.g., carboxy peptidase A and carbonic anhydrase (catalysis of biological system, CMA = Zn^{2+})
- c. **Extraction of Au and Ag:** The noble metals like Au and Ag are extracted from their ores through the formation of cyanide complexes e.g. $[Au(CN)_2]^-$ in aqueous solution and Au is precipitated by addition of Zn metal.
- d. **Purification of metals (Mond's process):** Impure Nickel is converted to $[Ni(CO)_4]$ which on decomposition gives pure Ni.
- e. When certain metals are present in toxic proportions in plant and animal system, they are removed by chelating ligand. e.g., excess of Cu and Fe is removed by the chelating ligands. D-Pencillamine and desferrioxime B via the formation of coordination compounds.
- f. Calcium dihydrogen salt of EDTA is used in treatment as an antidote for the Pb poisoning.
- g. EDTA is used in determining the hardness of H_2O . Ca^{2+} and Mg^{2+} can be selectively estimated because of difference in their K_a values. K_a value of Mg^{2+} complex $> K_a$ value of Ca^{2+} complex.
- h. Ziegler-Natta $[TiCl_4 + (C_2H_5)_3Al]$, a heterogenous catalyst (insoluble in the reaction medium) is used in the polymerisation of alkenes at atmospheric pressure and at ambient temperature (i.e., for the preparation of HDPE).
- i. Wilkinson's homogeneous catalyst $[RhCl(PPh_3)_3]$ (soluble in the reaction medium) is used in the hydrogenation of alkene.
- j. Many ligands (organic reagents) are used for the gravimetric estimation of number of metal ions.

S. No.	Metal ion to be estimated	Colour	pH	Organic Reagent
1.	Cu^{2+}	Red	pH = 9-10	Benzoin oxime (or cupron)
2.	Ni^{2+}	Red	pH = 9-10	DMG (Dimethylglyoxime)
3.	Fe^{3+}	Brown	-	1, 10-phenanthroline (ph)
4.	Al^{3+}	Blue	-	8-hydroxyquinoline
5.	Co^{2+}	Red	-	α -nitroso- β -naphthol

- k. **Test for S^{2-} ion:** The complex sodium nitroprusside, $Na_2[Fe^{II}(CN)_5NO^+]$ with S^{2-} gives violet colour.



- l. **Badecker reaction:** This reaction is used for test of sulphite ion.



- m. **Everitt's salt:** It is $K_2[Fe(CN)_6]$, obtained by reduction of Prussian blue.

- n. $[Fe^{II}(CN)_6]^{4-}$, $[Fe^{III}(CN)_6]^{3-}$ and SCN^- ions are used for the detection of various metal ions as shown below:

S. No.		Fe^{2+}	Fe^{3+}	Zn^{2+}	Cu^{2+}	Co^{2+}
1.	$[Fe^{II}(CN)_6]^{4-}$ Ferrocyanide ion	$Fe_2^{II}[Fe^{II}(CN)_6]$ Ferro-ferricyanide (White ppt.)	$Fe_4^{III}[Fe^{II}(CN)_6]_3$ Ferri-ferricyanide (Prussian blue)	$Zn_2[Fe^{III}(CN)_6]$ Bluish white ppt.	$Cu_2[Fe^{II}(CN)_6]$ Chocolate ppt.	-
2.	$[Fe^{III}(CN)_6]^{3-}$ Ferricyanide ion	$Fe_3^{II}[Fe^{III}(CN)_6]_2$ Ferro-ferricyanide (Turnbull's blue)	$Fe^{III}[Fe^{III}(CN)_6]$ Ferri-ferricyanide (Brown solution)	-	-	$Co_3^{II}[Fe(CN)_6]$ Reddish brown colour
3.	SCN^- Thiocyanate ion	-	$[Fe^{III}(SCN)_3]$ Blood red colour	-	-	$[Co^{II}(SCN)_4]^{2-}$ Blue colour

7.1 INTRODUCTION

The transition elements form a large number of **complex compounds** in which the metal atoms are bound to a number of anions or neutral molecules, such compounds are called **coordination compounds**. Chlorophyll, haemoglobin and vitamin B_{12} are coordination compounds of Mg, Fe and Co respectively. Variety of metallurgical processes, industrial catalysis and analytical reagents involve the use of coordination compounds. These compounds also find many applications, e.g. electroplating, textile dyeing and medicinal chemistry.

7.2 COMPLEX ION

It is defined as an electrically charged ion which consists of central metal atom/ion linked to group of molecule ions by means of coordinate bonds.

In general, complex ion is represented as $[ML_n]^{+x}$ where M is central metal ion, L is ligand bonded to M by means of coordinate bond. n is the coordination number of metal M and x is the net charge on the complex.

The main points of difference between a double salt and a complex compound are summarised in Table 7.1.

Table 7.1 Difference between a double salt and a complex compound

S. No.	Double salt	S. No.	Complex compound
1.	They exist only in the solid state. In aqueous solution, they dissociate completely into ions.	1.	They exist in solid state as well as in aqueous solution, because the complex ion does not dissociate into ions.
2.	They usually contain two simple salts in equimolar proportions.	2.	The simple salts from which they are formed may or may not be in equimolar proportions.
3.	They are ionic compounds and do not contain any coordinate bond.	3.	They may or may not be ionic but the complex part always contains coordinate bonds.
4.	The metal ions show their normal valency.	4.	The metal ion satisfies its two types of valencies called primary and secondary valencies (discussed in Section 7.5).
5.	They lose their identity in the solution.	5.	They retain their identity in the solution.
6.	The properties of double salts are same as those of their constituent compounds.	6.	The properties of these compounds are different from its constituents.

Note: Compounds like $K_3[Co(NH_3)_6]$, $K_4[Fe(CN)_6]$ etc. in which the complex ion is quite stable and almost does not dissociate into ions in the solution are called 'perfect complexes' or 'penetrating complexes'. Compounds like $K_2[Cd(CN)_4]$, in which the complex ion is not very stable and dissociates to greater extent to give simple ions are called 'imperfect or normal complexes'.

7.2.1 TYPES OF COMPLEX

1. **Cationic complex or positively charged complex:** Complex ion $[Cu(NH_3)_4]^{2+}$ in $[Cu(NH_3)_4]SO_4$, on ionisation gives $[Cu(NH_3)_4]^{2+}$ and SO_4^{2-} ions. $[Cu(NH_3)_4]SO_4$ carries net positive charge.
2. **Anionic complex or negatively charged complex:** Complex $K_3[Fe(CN)_6]$ gives three K^+ and $[Fe(CN)_6]^{3-}$ ions on ionisation. Complex ion $[Fe(CN)_6]^{3-}$ in $K_3[Fe(CN)_6]$ carries net negative charge.
3. **Neutral complex has cation and anion both as complex ion:** Complex $[Pt(NH_3)_4][PtCl_4]$ has $[Pt(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$ as cationic and anionic complex ion.
4. **Neutral complex having no net charge, e.g.** $[Ni(CO)_4]$.

7.3 SOME IMPORTANT TERMS USED IN COORDINATION COMPOUND

7.3.1 COORDINATION ENTITY AND COUNTER ION

A coordination entity constitutes a central atom/ion (usually a metal) to which are attached a fixed number of molecules/ions. It may be neutral or charged. This is also known as coordination sphere and is written inside $[]$ brackets, e.g. $[Ag(CN)_2]^-$. The ions present outside the coordination sphere constitute the **counter ion/ionisation sphere**.

The coordination entity and counter ions in the following coordination compounds:

$[Cr(NH_3)_6]Cl_3$, $K_4[Fe(CN)_6]$, $K_2[PtCl_4]$, $[Ni(CO)_4]$.

$K_2[Ni(CN)_4]$, $O_2[PtF_6]$, $Xe[PtF_6]$ are as shown below.

Coordination compound	Coordination entity	Type of coordination entity	Counter ion
$[Cr(NH_3)_6]Cl_3$	$[Cr(NH_3)_6]^{3+}$	Positively charged or cationic	$3Cl^-$
$K_4[Fe(CN)_6]$	$[Fe(CN)_6]^{3-}$	Anionic	$4K^+$
$K_2[PtCl_4]$	$[PtCl_4]^{2-}$	Anionic	$2K^+$
$Ni(CO)_4$	$[Ni(CO)_4]$	Neutral	—
$K_2[Ni(CN)_4]$	$[Ni(CN)_4]^{2-}$	Anionic	$2K^+$
$O_2[PtF_6]$	$[Pt^{+5}F_6]^-$	Anionic	O_2^{2-} (Dioxygenyl)
$Xe[PtF_6]$	$[Pt^{+5}F_6]^-$	Anionic	Xe^+

7.3.2 CENTRAL ATOM/ION

In the coordination entity, the atom/ion (usually a metal) to which one or more neutral or charged molecules are bound by means of coordinate bond formation in a definite geometrical arrangement around it, is called the central atom/ion.

The central atom/ion is also known as centre of coordination, e.g., the central atom/ion in the following compounds $[Co(NH_3)_6]Cl_3$, $K_3[Fe(CN)_6]$, $[PtCl_4(NH_4)_2]$, $[Ni(CO)_4]$ are as shown below.

Complex	Central ion
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	Co^{3+}
$\text{K}_3[\text{Fe}(\text{CN})_6]$	Fe^{3+}
$[\text{PtCl}_4(\text{NH}_3)_2]$	Pt^{4+}
$[\text{Ni}(\text{CO})_4]$	Ni^0

7.3.3 LIGANDS

Any molecule/ion which can donate at least a pair of electron to the central atom/ion to form a coordinate bond is known as ligand or coordinating group. Further in a ligand, the atom which actually donates the pair of electron is called as donor atom or ligating atom.

Complex formation can be explained in terms of Lewis acid–Lewis base concept. Central atom/ion which accepts electron pair(s) from ligands act as Lewis acid, whereas ligands which donate one or more pair of electron to central atom/ion acts as Lewis base. This also explains why transition elements having empty *d*-orbitals form coordination compounds easily.

7.3.3.1 Classification of Ligands

Ligands can be classified on the basis of denticity, i.e. the number of donor atoms present in the ligand molecule, which are forming coordinate bond with the central atom/ion, as follows:

- a. Monodentate or unidentate ligands:** If the ligand coordinates with central atom/ion using only one donor atom (irrespective of the number of donor atoms in it), it is known as monodentate ligand. These ligands may be neutral

molecules or ionic. Examples of monodentate ligands are given in Table 7.2.

Table 7.2 Some examples of monodentate or unidentate ligands

Neutral ligands		Negative ligands		Positive ligands	
$\leftarrow : \text{NH}_3$	Amine	F^\ominus	Fluorido	NO^\oplus	Nitrosonium
$\text{H}_2\ddot{\text{O}}: \rightarrow$	Aqua	Cl^\ominus	Chlorido	$\text{H}_2\text{N}^\oplus\text{—NH}_3$	Hydrazinium
$\leftarrow : \text{PH}_3$	Phosphine	$\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—O}^\ominus$	Acetato		
$\leftarrow : \text{CO}$	Carbonyl	N^{3-}	Nitrido		
$\leftarrow : \text{NO}$	Nitrosyl	NH_2^\ominus	Amido		

- b. Polydentate or multidentate ligands:** When two or more donor atoms present in the ligand coordinates with the central ion, the ligand is known as polydentate ligand. These may be bidentate, tridentate, tetradentate, pentadentate, hexadentate when it is coordinated with the central atom/ion at 2, 3, 4, 5, 6 sites respectively. In other words, one molecule/ion of these ligands makes 2, 3, 4, 5, 6 ($\text{M} \leftarrow \text{L}$) coordinate bonds respectively. Examples of polydentate ligands are given in Table 7.3.

Table 7.3 Some examples of polydentate ligands

Bidentate or didentate ligand		Charge	Donor atoms	IUPAC Name
i.	Ethylenediamine(en)	zero	Two N-atoms	1,2-Ethanediamine
ii.	2, 2-Dipyridyl (dipy)	zero	Two N-atoms	Dipyridyl
iii.	Oxalate ion	–2	Two O-atoms	Oxalato
iv.	Glycinate ion	–1	N, O	Glycinato
v.	Ortho-phenanthroline (Phen) or (ph)	zero	Two N-atoms	1, 10-Phenanthroline
vi.	Carbonate ion	–2	Two O-atoms	Carbonato

Tridentate or terdentate ligand:

i.	Diethylene triamine (dien)	$\text{H}_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2\text{NH}_2$ 	zero	Three N-atoms	[N-(2-aminoethyl)-1, 2-ethanediamine]
ii.	2, 2'-2'', Terpyridine (terpy)		zero	Three N-atom	Terpyridine

Tetradentate ligand:

Triethylene tetramine (trien)	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$ 	zero	Four N-atoms	[N, N'-bis-(2-aminoethyl)-1, 2-ethanediamine]
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Pentadentate ligand:

Ethylenediamine triacetate ion		-3	Two N and three O-atom	Ethylenediaminetriacetato
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Hexadentate ligand:

Ethylenediamine tetraacetate ion (edta ⁴⁻)		-4	Two N and four O-atom	Ethylenediaminetetraacetato
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Note: Polydentate ligands have flexible character. In simple terms, it is not necessary that all the donor atoms present in the polydentate ligand should form coordinate bond with central atom/ion. For example, ethylenediaminetetraacetic acid (EDTA) which is hexadentate ligand can also function as pentadentate or tetradentate ligand with certain metal ions.

c. Ambidentate ligands: Certain ligands have two or more donor atoms in their structure but while forming a complex only one donor atom/ligating site coordinates to the central atom/ion. Such ligands are known as ambidentate ligands, e.g. SCN^- , NO_2^- ion etc. When the ambidentate ligand having two different donor atoms coordinate to

the central atom/ion through either of its donor atoms, two different complexes are formed. These complexes are different because they have different structures. Such coordination compounds are called linkage isomers and the phenomenon is called linkage isomerism.

Examples of certain ambidentate ligands are given in Table 7.4.

Table 7.4 List of certain ambidentate ligands

Ambidentate ligand	Donor atom	Name	Linkage
a. NO_2^-	N	nitrito or nitrito-N	$\text{M} \leftarrow \text{NO}_2^-$
	O	isonitrito or nitrito-O	$\text{M} \leftarrow \text{:ONO}^-$
b. CN^-	C	cyano or cyano-C	$\text{M} \leftarrow \text{:CN}^-$
	N	isocyano or cyano-N	$\text{M} \leftarrow \text{:NC}^-$
c. SCN^-	S	thiocyanato or thiocyanato-S	$\text{M} \leftarrow \text{:SCN}^-$
	N	isothiocyanato or thiocyanato-N	$\text{M} \leftarrow \text{:NCS}^-$

d. Bridging ligand: Certain ligands e.g. N_2 or $\text{:N}\equiv\text{N:}$, $\text{NH}_2 - \text{NH}_2$, OH^- , NH_2^- , NH_2^+ , O^{2-} , Cl^- , SO_4^{2-} , NO_2^- etc. are monodentate ligands, they also act as bidentate ligands when they are attached to two separate metal atoms making a bridge between them. Such ligands are

called bridging ligands and the complexes thus formed are called **bridged** or **polynuclear complexes**. A bridging ligand must have at least two lone pairs of electrons which the ligand uses to get coordinated to two or more metal atoms. The polynuclear complex formed can be dinuclear, trinuclear etc.

7.3.3.2 Chelation

When coordination of two or more donor atoms from a polydentate ligand to a single central atom/ion takes place forming a closed or cyclic ring structure, it is called chelation and the ligand a chelating ligand. The close ring compound thus formed is called chelate or metal chelate (Chelos, Greek word means 'crab').

Some important characteristics of chelates:

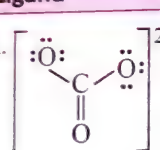
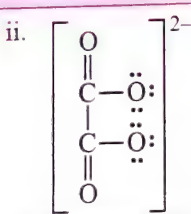
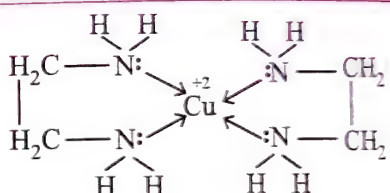
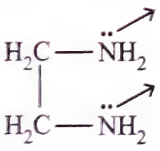
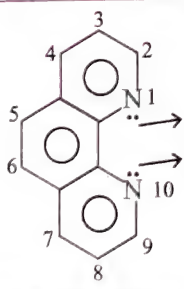
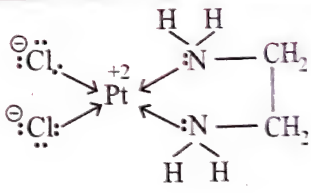
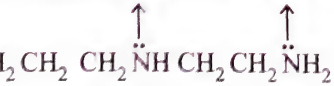
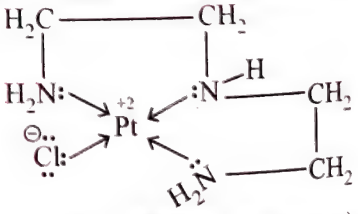
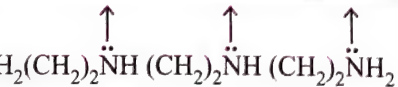
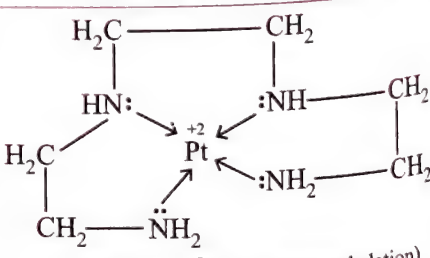
- Chelating effect:** Chelating ligands form more stable complexes than the monodentate analogs. The complex ion/compound having such ligands does not dissociate easily.
- Formation of rings:** Generally the chelate complexes with 5- or 6-membered rings are more stable. Out of these, 5-membered rings are very stable when they involve saturated ligands, e.g., ethylenediamine which contains 5-membered stable ring structure. On the other hand 6-membered ring structures acquire maximum stability when they involve unsaturated ligands containing conjugate double bonds.
- Steric hindrance:** Ligands with large groups form unstable rings than the ligands with smaller groups due to steric hindrance.

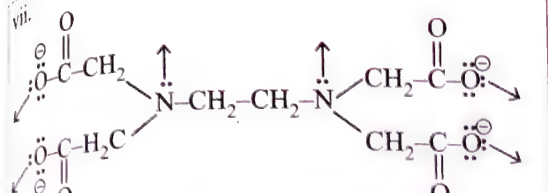
d. Number of rings: The complex compound having maximum number of rings formed with the ligands is most stable. For example, a complex $[M(en)_3]^{3+}$ is less stable than a complex $[M(EDTA)]^\ominus$ because in the former there are 3 rings while in the latter 5 rings.

e. Entropy effect: The stability of the chelate complex is explained on the basis of entropy effect. To elaborate, let us take an example of ethylene diamine ligand (en). When one end of 'en' is coordinated, the probability of coordination of the other end is high because this end is bound to stay close to the central atom/ion. This shows that it is easier to form a chelate ring than forming coordinate bonds with two independent molecules. Thermodynamically, the increased stability due to chelation can be attributed to an increase in the degree of freedom of the system. Large changes in entropy but only small heat of reaction generally accompany the chelation process.

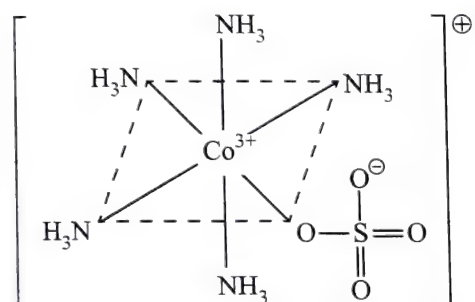
The **number of donor atoms/ligating atoms** present in the ligand molecule which are coordinating with the central atom/ion indicates the **denticity** of the ligand (Table 7.5).

Table 7.5 Some examples of chelating ligands and number of donor atoms

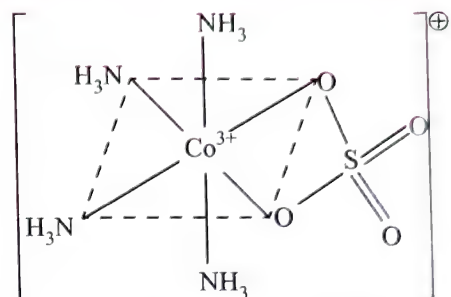
Ligand	Type of ligand	Donor atom	Examples
i.  ii.  Carbonate ion Oxalate ion or $[OX]^{2-}$	Bidentate or Didentate	2-O atoms	 Bidentate chelation
iii.  iv.  Ethylene diamine (en) OR [1,2-ethanediamine] Ortho-phenanthroline(ph) (or) 9,10-phenanthroline	Bidentate or Didentate	2-N atoms	 [PtCl ₂ (en)]
v.  Diethylene triamine (dien) or [N-(2-aminoethyl)-1,2-ethane diamine]	Tridentate or Terdentate	3-N atoms	 [PtCl(dien)] ⁺ (Tridentate chelation)
vi.  Triethylene tetraamine. (trien) Or [N, N'-bis-(2-aminoethyl)-1,2-ethanediamine]	Tetradentate	4-N atoms	 [PtCl(trien)] ²⁺ (Tetradentate chelation)

<p>vii.</p>  <p>Ethylenediamine tetraacetate ion (EDTA)⁴⁻</p>	Hexadentate	4-O-atoms and 2-N atoms	
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f. **Flexidentate ligands:** Certain ligands have more than one donor atoms like SO_4^{2-} , CO_3^{2-} , etc. which have more than one donor site/ligating atoms. Such ligands can behave as monodentate ligand in one complex and bidentate in another complex. Such ligands which show variable denticity in different complexes are known as flexidentate ligands. (It is not necessary for a polydentate ligand to use all its donor atoms for coordination.) For example:



$[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]^{\oplus}$ ion (SO_4^{2-} as monodentate ligand)



$[\text{Co}(\text{NH}_3)_4(\text{SO}_4)]^{\oplus}$ ion (SO_4^{2-} as bidentate ligand)

7.4 COORDINATION NUMBER

The number of ligating atoms (of the ligands) that are directly bound to the central atom/ion is known as coordination number. It is equal to the number of sigma bonds formed between the ligands and central atom/ion. π -Bonds, if any, between the ligating atom and the central atom/ion are not considered for the consideration of coordination number. Like CO, CN^{\ominus} and N_2 may involve both σ and π bonding between the central atom/ion and the ligating atom, it is only number of σ bonds formed which are considered in determining the coordination number (Table 7.6).

Table 7.6 Coordination number (CN) of some central metal atoms/ions (Note: CN = Denticity \times no. of ligands)

A. Some examples of unidentate ligands

S.No.	Central metal atom/ions	CN	Complexes	Ligands
1.	Ag^{\oplus} , Cu^{\oplus} , Au^{\oplus}	2	$[\text{Ag}(\text{NH}_3)_2]^{\oplus}$	NH_3
2.	Hg^{2+}	3 and 4	$[\text{HgI}_3]^{\ominus}$, $[\text{HgI}_4]^{2-}$	I^{\ominus}
3.	Cu^{2+} , Pt^{2+} , Ni^{2+} , Mn^{2+} , Pd^{2+} , Zn^{2+} , Ni^0	4	$[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{PtCl}_4]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{MnBr}_4]^{2-}$, $[\text{PdCl}_4]^{2-}$, $[\text{ZnCl}_4]^{2-}$, $[\text{Ni}(\text{CO})_4]$	NH_3 , Cl^{\ominus} , CN^{\ominus} , Br^{\ominus} , Cl^{\ominus} Cl^{\ominus} and CO respectively
4.	Co^{2+}	4 and 5	$[\text{Co}(\text{CN})_5]^{3-}$, $[\text{CoCl}_4]^{2-}$	CN^{\ominus}
5.	Fe^0	5	$[\text{Fe}(\text{CO})_5]$	CO
6.	Fe^{2+} , Fe^{3+} , Co^{3+} , Pt^{4+} , Cr^{3+} , Cr^0 , Ni^{2+} , Ir^{3+}	6	$[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{PtCl}_6]^{2-}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{CO})_6]$, $[\text{NiF}_6]^{4-}$, $[\text{Ir}(\text{NH}_3)_6]^{3+}$	CN^{\ominus} , CN^{\ominus} , NH_3 , Cl^{\ominus} , H_2O , CO, F^{\ominus} and NH_3 respectively
7.	Mo^{4+}	7	$[\text{Mo}(\text{CN})_7]^{3-}$	CN^{\ominus}
8.	W^{4+}	8	$[\text{W}(\text{CN})_8]^{4-}$	CN^{\ominus}

B. Some examples of complexes with multidentate ligands.

- $[\text{Co}(\text{en})_3]^{3+}$
CN = Didentate \times no. of ligands = $2 \times 3 = 6$
- $[\text{Cr}(\text{dien})_2]^{3+}$
CN = Tridentate \times no. of ligands = $3 \times 2 = 6$

- $[\text{Mg}(\text{trien})\text{Cl}_2]$
CN = Tetradentate \times no. of ligands = $4 \times 1 + 2 = 6$
- $[\text{Mg}(\text{EDTA})]^{2-}$
CN = Hexadentate \times no. of ligands = $6 \times 1 = 6$

7.4.1 OXIDATION NUMBER OF CENTRAL ATOM/ION

Oxidation number of the central atom in the coordination entity is defined as the charge it would bear if all the ligands were removed along with the electron pairs that were shared with the central atom. It is represented in numerals (Table 7.7).

Table 7.7 Examples of important terms used in describing coordination compounds

Coordination compound	Central metal atom	Ligands	Oxidation no.	Geometrical shape
Ni(CO)_4	Ni	four CO	Zero	Tetrahedral
$[\text{NiCl}_4]^{2-}$	Ni	four Cl^\ominus	II (2+)	Tetrahedral
$[\text{Ni(CN)}_4]^{2-}$	Ni	four CN^\ominus	II (2+)	Tetrahedral
$[\text{Ni(H}_2\text{O)}_6]^{2+}$	Ni	six H_2O	II (+2)	Octahedral
$[\text{Co(NH}_3)_6]^{3+}$	Co	six NH_3	III (+3)	Octahedral
$[\text{Co(CN)}_5\text{F}]^{3-}$	Co	five CN^\ominus one F^\ominus	III (+3)	Octahedral
$[\text{Ag(NH}_3)_2]^+$	Ag	two NH_3	I (+1)	Linear
$[\text{Cu(NH}_3)_4]^{2+}$	Cu	four NH_3	II (+2)	Square planar

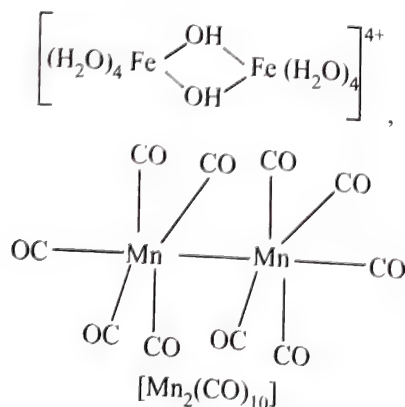
7.4.2 HOMOLEPTIC AND HETEROLEPTIC COMPLEXES

- Homoleptic complexes are those complexes in which central atom is coordinated with only one kind of ligand, e.g., $[\text{Fe(CN)}_6]^{3-}$.
- Heteroleptic complexes are those in which central atom is coordinated with more than one kind of ligands, e.g., $[\text{Fe(H}_2\text{O)}_5\text{NO}]^{2+}$.

7.4.3 HOMONUCLEAR AND POLYNUCLEAR OR BRIDGED COMPLEXES

Complexes in which only one metal is present are known as homonuclear complexes, e.g., $[\text{Co(NH}_3)_6]^{3+}$ and $[\text{Co(NH}_3)_4\text{Cl}_2]^+$.

Complexes in which more than one metal atom is present are known as polynuclear or bridged complexes. These complexes are formed by bridging ligands. These complexes formed can be dinuclear, trinuclear etc. For example,



Various terms discussed above may be illustrated by taking some examples of coordination compounds, e.g.

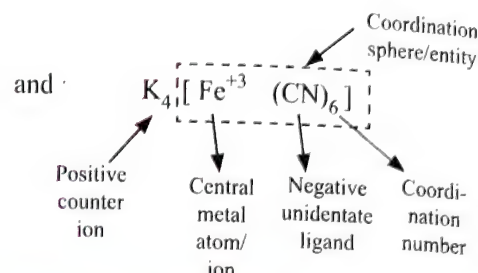
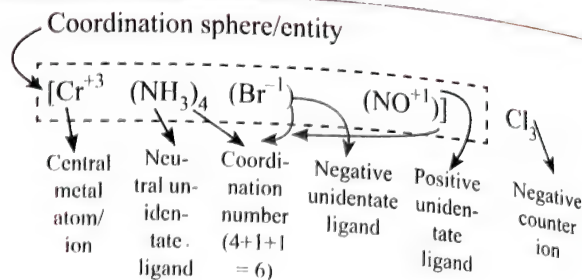


ILLUSTRATION 7.1

Why NH_3 form coordinate complex, while the isoelectronic species CH_4 does not.

Sol. NH_3 has a lone pair of electron on N hence, it can act as a ligand and form coordinate complex whereas in CH_4 , C has no lone pair of electrons present on it, hence it cannot form complex.

ILLUSTRATION 7.2

Calculate the oxidation number of Ni ion $[\text{Ni(H}_2\text{O)}_6]^{2+}$.

Sol. Oxidation number is calculated as follows:

Charge on complex ion = +2

Let charge on Ni = x

Charge on H_2O = 0

$\Rightarrow x + 6 \times (0) = +2$

$\Rightarrow x = +2$

Hence oxidation number of Ni is II.

ILLUSTRATION 7.3

Calculate the oxidation number of Ni in $\text{K}_2[\text{Ni(CN)}_4]$.

Sol. Let the charge on Ni be x

Charge on $\text{CN}^\ominus = -1$

$\text{K}_2[\text{Ni(CN)}_4] \rightarrow 2\text{K}^+ + [\text{Ni(CN)}_4]^{2-}$

Charge on complex ion, $[\text{Ni(CN)}_4]^{2-} = -2$

$\Rightarrow x + 4 \times (-1) = -2$

$\Rightarrow x = +2$

\therefore Oxidation number of Ni is II.

ILLUSTRATION 7.4

What is the coordination number and oxidation state of Al in the complex $[\text{Al(H}_2\text{O)}_4(\text{OH})_2]^+$?

Sol. Coordination number of Al in $[\text{Al(H}_2\text{O)}_4(\text{OH})_2]^+$ is 6. To calculate oxidation state of Al in $[\text{Al(H}_2\text{O)}_4(\text{OH})_2]^+$ Charge on H_2O is 0 (zero) and on OH is -1.

Let the charge on Al be x .

$$x + 0 \times 4 + (-1) \times 2 = +1$$

$$x = +3$$

\therefore Oxidation state of Al in $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^{\oplus}$ is +3.

ILLUSTRATION 7.5

In the complex, $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]\text{Br}$, identify

- Ligands and their charges.
- Charge of the central ion in the complex.
- What would happen if AgNO_3 is added to the compound at 0°C .

Sol. In complex $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]\text{Br}$, the complex ion is $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]^{\oplus}$

- Ligands are $5\text{H}_2\text{O}$ and Cl^{\ominus} .
 H_2O is neutral ligand, whereas Cl^{\ominus} has one negative charge.
- Let the charge on the central ion in the complex be x .
 $\therefore x + 0 \times 5 + (-1) = +1$
 $x = +2$
 i.e. charge on Fe in $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]^{\oplus}$ is +2.
- $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]\text{Br} + \text{AgNO}_3 \rightarrow [\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]\text{NO}_3 + \text{AgBr}$
 On addition of AgNO_3 to the compound one mole of AgBr will be precipitated.

coordination entity is written outside the square bracket as a right superscript. For example $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$ etc.

- Structural modifiers such as *cis*, *trans* etc. if present are given in lower case as an italicised prefix. It is connected to the formula by a hyphen.
- Finally a counter ion could be added to the coordination entity to form coordination compound. If counter ion is positively charged species, it is written in front of the formula of coordination entity, and if it is a negatively charged species, it is written after the formula of the coordination entity. No space is left between the counter ion and the coordination entity.

Note:

- A single letter symbol always precedes a two-letter symbol with the same initial letter, e.g. B before Be; O before OH, the group NH_3 is treated as a single symbol and so is listed after Na.
- Where the entities to be arranged in a formula are polyatomic:
 - The order of citation is decided by selecting the first symbol in the formula of a polyatomic group. For example, C_5H_5 , SCN , NO_2 and OH are ordered under C, S, N and O respectively.
 - If the first symbols are the same, the symbol with the lesser right index is cited first, e.g. NO_2 precedes N_2O_2 .
 - If this still does not discriminate, the subsequent symbols are used alphabetically and numerically to define the order, e.g. NH_2 precedes NO_2 which precedes NO_3 .
 - To summarise and exemplify, the order of citation of some nitrogen-containing compounds is:
 N^{3-} , NH_2^{\ominus} , NH_3 , NO_2^{\ominus} , NO_3^{\ominus} , $\text{N}_2\text{O}_2^{2-}$, N_3^{\ominus}

For example,

- $[\text{Al}(\text{OH})(\text{OH}_2)_5]^{2+}$
- $[\text{PtCl}_2(\text{NH}_3)(\text{py})]$
- $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2-}$
- $[\text{PtBrCl}(\text{NH}_3)(\text{NO}_2)]^{\ominus}$
- $[\text{Co}(\text{en})\text{F}_2(\text{NH}_3)_2]^{\oplus}$, is written as
 $[\text{CoF}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2(\text{NH}_3)_2]^{\oplus}$

- Ionic charges and oxidation numbers: If the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square bracket as a right superscript, with the number before the sign. The oxidation number of a central atom may be represented by a Roman numeral, which should be placed as a right superscript on the element symbol.

Examples:

- $[\text{PtCl}_6]^{2-}$
- $[\text{Cr}^{\text{III}}\text{Cl}_3(\text{OH}_2)_3]$
- $[\text{Cr}(\text{OH}_2)_6]^{3+}$
- $[\text{Fe}^{\text{II}}(\text{CO})_4]^{2-}$
- $[\text{Cr}^{\text{III}}(\text{NCS})_4(\text{NH}_3)_2]^{\ominus}$

7.5.2 RULES FOR WRITING THE NAME OF MONONUCLEAR COORDINATION COMPOUND

The rules as recommended by IUPAC (International Union of Pure and Applied Chemistry), revised in 2005, being followed while naming a mononuclear coordination compound are as follows:

7.5 NOMENCLATURE OF COORDINATION COMPOUNDS

Coordination compounds are considered to be produced by addition reactions. They are therefore named on the basis of 'additive principle'. The name is built up around the central atom just as the coordination entity is built up around the central atom.

For example, addition of ligands to a central atom:

$\text{Co}^{2+} + 6\text{NH}_3 \longrightarrow [\text{Co}(\text{NH}_3)_6]^{2+}$, addition of ligands name to the central atom/ion is hexaamminecobalt(III).

7.5.1 RULES FOR WRITING THE FORMULAE FOR MONONUCLEAR COORDINATION COMPOUND

Sequence of symbols within the coordination formula is governed by the following rules:

- The central atom is listed first followed by the ligands.
- The ligands are listed in alphabetical order of the ligating atoms (charge of the ligand is not considered when deciding the order and the charge of the ligand is not written in the formula).
- The formula for the entire coordination entity is enclosed in square brackets.
- When the ligands are polyatomic (i.e. contain more than one atom) their formulae are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.
- No space is kept between representations of ionic species within the formula.
- When the formula of a charged coordination entity is to be written without the counter ion, the charge of the

- i. If the coordination compound is molecular or non-ionic a single word name is given.
- ii. If the coordination compound is in the form of salt or ionic, name of the cation is given first, followed by the name of the anion in accordance with the usual nomenclature scheme. A space is left between the cationic and anionic part.
- iii. In the coordination entity, name of the ligand is written first followed by the name of central metal atom/ion.
- iv. Order of naming ions: The positive ion (cation) is named first followed by the negative ion (anion) irrespective of whether cation is complex or anion is complex. The complex part is written as one word e.g., $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, hexaamminecobalt(III) chloride.
- v. **Naming of ligands:** Different types of ligands are named differently (refer to Table 7.8).
 - a. **Neutral ligands:** These type of ligands have no special ending and are used as such except for NH_3 (ammine), H_2O (aqua), CO (carbonyl), CS (thiocarbonyl) and NO (nitrosyl).
 - b. **Positive ligands:** These type of ligands are used as such. These generally end in -ium, e.g., $\text{H}_2\text{N} - \text{NH}_3^+$

(hydrazinium), NO^+ (nitrosonium), NO_2^+ (nitronium) etc.

- c. **Negative ligands (organic or inorganic):** These type of ligands end in '-O' e.g., CN^- (cyano), Cl^- (chloro), NO_2^- (nitro), O^{2-} (oxo), O_2^{2-} (peroxo), O_2^- (superoxo). If the name of the anionic ligands ends in -ide, -ite or -ate, the last 'e' is replaced by 'O' giving -ido, -ito or -ato e.g. SO_4^{2-} (sulphato), NH_2^- (amido), ONO^- (nitrito) etc.

- d. **Organic ligands:** Organic free radicals are given their own names, e.g. CH_3^\bullet (methyl), $(\text{C}_2\text{H}_5)^\bullet$ (ethyl). For organic neutral molecules, their names are used. e.g., $\text{P}(\text{C}_6\text{H}_5)_3$, triphenyl phosphine, $\text{C}_6\text{H}_5\text{N}$ pyridine (py) etc. (refer Table 7.8).

Note: Enclosing marks '()' are required for (a) neutral and cationic ligand names (however, common ligands such as aqua, ammine, carbonyl, nitrosyl, methyl, ethyl, etc., do not require enclosing marks, unless there is ambiguity); (b) for inorganic anionic ligands containing numerical prefixes (such as triphosphato); (c) for any compositional name (such as carbon disulfide); (d) for any substituted organic ligand (even if there is no ambiguity in its use); (e) and wherever necessary to avoid ambiguity.

Table 7.8 List of neutral, positive and negative ligands

Denticity	Name	Ligand	Charge	Name of the ligand in the complex	Donor atom
Neutral ligands	Water	H_2O	0	Aqua/aquo	O
	Ammonia	NH_3	0	Ammine	N
	Carbon monoxide	CO	0	Carbonyl	C
	Nitrogen oxide	NO	0	Nitrosyl	N
	Thiocarbonyl	CS	0	Thiocarbonyl	S
	Thionitrosyl	NS	0	Thionitrosyl	N
Monodentate	Pyridine (py)	$\text{C}_5\text{H}_5\text{N}$	0	Pyridine (py)	N
	Methyl amine	CH_3NH_2	0	Methylamine	N
	Dinitrogen	N_2	0	Dinitrogen	N
	Dioxygen	O_2	0	Dioxygen	O
	Phosphine	PH_3	0	Phosphine	P
	Urea	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{C}-\text{NH}_2 \end{array}$	0	Urea	O
	Thio-urea(tu)	$\begin{array}{c} \text{S} \\ \parallel \\ \text{H}_2\text{N}-\text{C}-\text{NH}_2 \end{array}$	0	Thio-urea	S
	Triphenylphosphine	Ph_3P	0	Triphenylphosphine	P
Bidentate	Acetone	CH_3COCH_3	0	Acetone	O
	Ethylenediamine (en) (a bidentate ligand)	$\text{NH}_2(\text{CH}_2)_2\text{NH}_2$	0	Ethylenediamine (en)	2 N-atoms
Tridentate	Diethylene triamine (dien)	$\begin{array}{c} \text{H}_2\text{C}-\ddot{\text{N}}\text{H}-\text{CH}_2 \\ \quad \quad \\ \text{H}_2\text{C}-\ddot{\text{N}} \quad \ddot{\text{N}}-\text{CH}_2 \\ \quad \quad \\ \text{H}_2 \quad \text{H}_2 \end{array}$	0	Diethylene triamine (diene)	3 N-atoms

Tetradentate	Triethylene tetramine (trien)	$\begin{array}{c} \text{H}_2\text{C}-\ddot{\text{N}}\text{H}(\text{CH}_2)_2\ddot{\text{N}}\text{H}_2 \\ \\ \text{H}_2\text{C}-\ddot{\text{N}}\text{H}(\text{CH}_2)_2\ddot{\text{N}}\text{H}_2 \end{array}$	0	Triethylene tetramine (trien)	4N-atoms
		Positive ligands			
Monodentate	Nitrosonium ion	NO^{\oplus}	+1	Nitrosonium	N
	Nitronium ion	NO_2^{\oplus}	+1	Nitronium	N
	Hydrazinium ion	$\text{NH}_2\text{NH}_3^{\oplus}$	+1	Hydrazinium	N
		Negative ligands			
Monodentate	Hydride ion	H^{\ominus}	-1	Hydrido	H
	Oxide ion	O^{2-}	-2	Oxo	O
	Peroxide ion	O_2^{2-}	-2	Peroxo	O
	Perhydroxide ion	$\text{O}_2\text{H}^{\ominus}$	-1	Perhydroxo	O
	Hydroxide ion	OH^{\ominus}	-1	Hydroxo	O
	Fluoride ion	F^{\ominus}	-1	Fluoro (fluorido)	F
	Chloride ion	Cl^{\ominus}	-1	Chloro (chlorido)	Cl
	Bromide ion	Br^{\ominus}	-1	Bromo (bromido)	Br
	Iodide ion	I^{\ominus}	-1	Iodo (iodido)	I
	Acetate ion	$\text{CH}_3\text{COO}^{\ominus}$	-1	Acetato (acetatido)	O
	Cyanide ion	CN^{\ominus}	-1	Cyano (cyanido)	C
	Isocyanide ion	$\text{N}^{\oplus}\equiv\text{C}^{\ominus}$	-1	Isocyano	N
	Sulphite ion	SO_3^{2-}	-2	Sulphito	O
	Sulphide ion	S^{2-}	-2	Sulphido or thio	S
	Hydrogensulphite ion	HSO_3^{\ominus}	-1	Hydrogensulphito	O
	Amide ion	NH_2^{\ominus}	-1	Amido	N
	Imide ion	NH^{2-}	-2	Imido	N
	Nitrate ion	NO_3^{\ominus}	-1	Nitrato	N
	Nitro ion	$\text{NO}_2^{\ominus} (\text{M} \leftarrow \text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array})$	-1	Nitro (nitrito-N)	N
	Nitrito ion	$\text{ONO}^{\ominus} (\text{M} \leftarrow \text{O}-\text{N}=\text{O})$	-1	Nitrito (nitrito-O)	O
	Nitrido ion	N^{3-}	-3	Nitrido	N
	Azide ion	N_3^{\ominus}	-1	Azido	N
	Cyanate ion	CNO^{\ominus}	-1	Cyanato	O
	Isocyanate ion	OCN^{\ominus}	-1	Isocyanato	N
	Thiocyanate ion	$^{\ominus}\text{SCN} (\text{M} \leftarrow \text{SCN})$	-1	Thiocyanato	S
	Isothiocyanate ion	$^{\ominus}\text{NCS} (\text{M} \leftarrow \text{NCS})$	-1	Isouthiocyanato	N
	Hydrogen carbonate ion	HCO_3^{\ominus}	-1	Hydrogencarbonato	O
Bidentate	Acetyl acetate ion	$\begin{array}{c} \text{CH}_3\text{C}-\text{CH}=\text{C}-\text{CH}_3 \\ \quad \\ \text{O} \quad \text{O}^{\ominus} \end{array}$	-1	Acetylacetato (Acac)	2 O-atom
	Glycinate ion	$\text{NH}_2-\text{CH}_2-\text{COO}^{\ominus}$	-1	Glycinato(gly)	1 N-atom and 1 O-atom
	Sulphate ion	SO_4^{2-}	-2	Sulphato	2 O-atom
	Thiosulphate ion	$\text{S}_2\text{O}_3^{2-}$	-2	Thiosulphato	2 O-atom

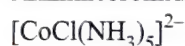
	Dimethylglyoxime	$\begin{array}{c} \text{O}^- \\ \\ \text{CH}_3\text{C}=\text{N}: \\ \\ \text{CH}_3\text{C}=\text{N}: \\ \\ \text{OH} \end{array}$	-1	Dimethylglyoximate	2 N-atom
	Oxalate ion	$\text{C}_2\text{O}_4^{2-}$	-2	Oxalato	2 O-atom
	Carbonate ion	CO_3^{2-}	-2	Carbonato	2 O-atom
Pentadentate	Ethylenediamine triacetate ion	$\begin{array}{c} \text{CH}_2-\ddot{\text{N}}(\text{CH}_2\text{COO}^-)_2 \\ \\ \text{CH}_2-\ddot{\text{N}}\text{HCH}_2\text{COO}^- \end{array}$	-3	(EDTA ³⁻)	2 N-atoms and 3 O-atoms
Hexadentate	Ethylenediamine tetraacetate ion	$\begin{array}{c} \text{CH}_2-\ddot{\text{N}}(\text{CH}_2\text{CO}_2^-)_2 \\ \\ \text{CH}_2-\ddot{\text{N}}(\text{CH}_2\text{CO}_2^-)_2 \end{array}$	-4	(EDTA ⁴⁻)	2 N-atoms and 4 O-atoms

- vi. Within the coordination sphere, if more than one kind of ligands are present, they are listed in alphabetical order (irrespective of their charge) before the name of the central atom. Numerical prefixes which indicate the number of ligands are not considered in determining that order.

For example,



Amminebromidochloridonitroplatinate (II)



Pentaamminechloridocobaltate (III)

- vii. **Prefixes:** Number of ligands in the coordination entity is indicated as numerical prefix. Two types of numerical prefixes are used.

- a. di, tri, tetra, penta etc. (mono is generally omitted). Multiplicand is not enclosed in parentheses. This is used for simple ligands.

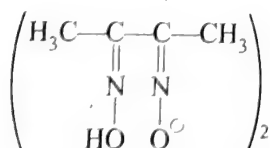
For example, $2 \text{Cl}^- \longrightarrow$ dichlorido

$3 \text{NH}_3 \longrightarrow$ triammine

- b. bis, tris, tetrakis, pentakis etc. Multiplicand is enclosed in parenthesis. This is used for complex ligands, i.e., when the name of the ligand is lengthy or complicated (polysyllabic or multiplicative prefixes are already present in the ligand)

$(\text{CH}_3\text{NH}_2)_2$ Bis(methylamine)

$\left(\begin{array}{c} \text{CH}_2-\text{NH}_2 \\ | \\ \text{CH}_2-\text{NH}_2 \end{array} \right)_3$ Tris (1, 2-ethanediamine)



Bis(dimethylglyoximate)

- viii. The final vowel of the numerical prefix is not omitted. (mono is an exception)

mono + oxide \longrightarrow (monoxide)

Example: $(\text{NH}_3)_4$ Tetraammine
 $(\text{O}^{2-})_4$ Tetraoxide

The complex $[\text{CoCl}_2(\text{NH}_3)_4]^\oplus$ is

Tetraamminedichloridocobalt (III)

- ix. The oxidation state of the central metal atom/ion is expressed in roman numerals, which is added at the end of the name of metal atom/ion and enclosed in bracket. No positive sign is used. For example,

$[\text{Co}(\text{NH}_3)_6]^{2+}$ Hexaamminecobalt (III) ion

- x. When the coordination entity is anionic or negatively charged the name of the central metal atom/ion ends with suffix 'ate', i.e., the name of coordination entity ends in 'ate'.

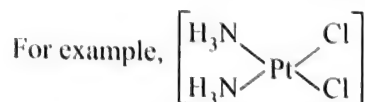
For certain elements their latin name is used. e.g.,

Example	Name in positive/neutral complex	Name in anionic or negative complex
Ag	Silver	Argentate
Pb	Lead	Plumbate
Au	Gold	Aurate
Hg	Mercury	Mercurate or hydrazinate
Ni	Nickel	Nickelate
Fe	Iron	Ferrate

- xi. If the coordination entity is positively charged or neutral, it has no special ending. For example,

$[\text{Co}(\text{CN})_6]^{3-}$ Hexacyanocobaltate (III) ion.

- xii. **Stereochemical descriptors:** For coordination number greater than one, different geometrical arrangements of the atoms attached to the central metal ion are possible. A descriptor is used to differentiate between isomers. The descriptor is indicated as an italicized prefix, in lower case. It is connected to the name by a hyphen.

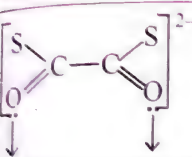
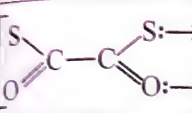
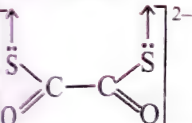


is named as *cis*-diaminedichloridoplatinum (II)

- xiii. **Naming of the optical isomers:** Dextro and Levorotatory optically active compounds are respectively designated either by (+) and (-) or by *d*- and *l*; e.g., dextrorotating

$K_3[Cr(ON)_3]$ is named as potassium (+) trioxalatochromate (III) or potassium *d*-trioxalatochromate (III).

iv. **Naming of the linkage isomers:** If necessary, the point of attachment of the ligand to the central metal is expressed by the symbol of element attached in italics after the name of the ligand and separated by a hyphen.

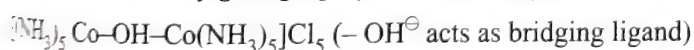
Ligand	Donor atom	Name of the ligand
$\leftarrow :SCN^\ominus$	S	Thiocyanato-S
$\leftarrow :NCS^\ominus$	N	Thiocyanato-N
$\leftarrow :CN^\ominus$	C	Cyano-C
$\leftarrow :NC^\ominus$	N	Cyano-N
	O, O	Dithioxalato-O-O'
	O, S	Dithioxalato-O-S
	S, S	Dithioxalato-S-S'

For example: $[Co(NH_3)_5(NO_2)]^{2+}$ has two isomeric forms having red and yellow colours.

1. The red colour isomer $[Co(NH_3)_5(ONO_2)]^{2+}$ is named as pentaamminenitrito-O-cobalt (III).
2. The yellow isomer $[Co(NH_3)_5(NO_2)]^{2+}$ is named as pentaamminenitrito-N-cobalt (III)

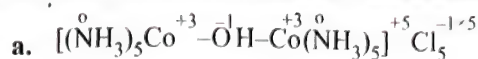
7.5.3 BRIDGING LIGAND

It is defined as the ligand which bounds to two or more central atoms simultaneously giving a polynuclear complex, e.g.



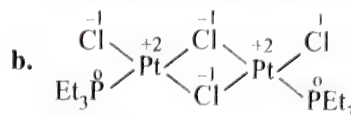
When bridging ligand is present within the complex, following points are noted for the nomenclature of these complexes:

- Bridging ligand is expressed by greek letter ' μ ' which is added immediately before the name of the ligand and separated by a hyphen.
- The number of bridging ligands are expressed as:
 - di- μ (Two bridging ligands)
 - Tri- μ (Three bridging ligands)
 - bis- μ (Two polysyllabic bridging ligands)
- The bridging ligands along with non-bridging ligands are generally written in alphabetical order unless the symmetry of the complex permits the simpler name by the use of multiplicative prefixes.
- If the same type of ligand is acting as bridging as well as non-bridging ligand, the bridging ligand is expressed first. Following examples illustrate the above points:

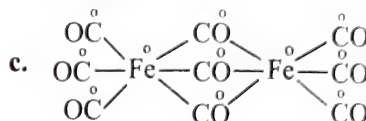


is given the name as

μ -hydroxo-bis (pentaamminecobalt (III)) chloride



(*cis*-di- μ -chloridobis(chlorotriethylphosphine)platinum (II))



Tri- μ -carbonyl bis(tricarbonyliron(0))

7.5.4 POLYNUCLEAR COMPLEXES

Polynuclear complexes having M-M bond can be symmetrical or unsymmetrical. In such complexes the rules followed to write the name of the complex are as follows:

- In case of symmetrical complex, the names are generally given with the use of multiplicative prefixes like di-, tri-, tetra-, etc.

For example, $[(\overset{0}{CO})_5Mn-\overset{0}{Mn}(\overset{0}{CO})_5]$

Bis (pentacarbonylmanganese(0))

- In case of unsymmetrical complex, one of the central atom and ligands bonded to it are considered as the ligand to the other central atom.

For example, $[(\overset{0}{CO})_4\overset{0}{CO}-\overset{0}{Re}(\overset{0}{CO})_5]$

Pentacarbonyl (tetracarbonylcobalt(0))ruthenium (0)

7.5.5 STABLE OXIDATION STATE (OS): SOME OF THE TRANSITION METALS OF THE THREE SERIES

These stable OS would be helpful to find the oxidation states of the metal ions while naming complexes having cation and anion both as complexes.

i. First transition series:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2, +3	+2, +3	+2, +3	+2, +3	+2, +3	+2, +3	+2, +3	+1, +2	+2
	+4	+4, +5	+6	+4, +7					

ii. Second transition series:

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	+4	+3, +5	+6	+4, +6	+3	+3	+2, +4	+1	+2
				+7					

iii. Third transition series:

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	+4	+5	+6	+4, +6	+3, +4	+1, +3	+2, +4	+1, +3	+1, +2
				+7	+6	+4			

Table 7.9 IUPAC name of some complexes

a.	Complex cation	IUPAC name
1.	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	Hexaamminecobalt(III) chloride
2.	$[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{NO}_3$	Tetraaquadichloridochromium (III) nitrate
3.	$[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]\text{NO}_3$	Tetraamminechloridonitrito-N-cobalt(III) nitrate
4.	$[\text{Cr}(\text{en})_3]\text{Cl}_3$	Tris(1,2-ethanediamine)chromium(III)chloride
5.	$[\text{CoCl}_2(\text{en})_2](\text{SO}_4)_2$	Dichlorido(1,2-ethanediamine)cobalt(II) sulphate
6.	$\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$	Sodium trioxalatoferrate(III)
7.	$[\text{CoBr}(\text{NH}_3)_4(\text{H}_2\text{O})](\text{NO}_3)_2$	Tetraammineaquabromidocobalt(III) nitrate
8.	$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	Hexaaquachromium(III) chloride
9.	$[\text{CoCl}(\text{ONO})(\text{en})_2]^{\oplus}$	Chloridobis(1,2-ethanediamine)nitrito-O-cobalt(III) ion
10.	$[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}$	Tetraaquadichloridochromium(III) chloride
11.	$[\text{Co}(\text{CO}_3)(\text{NH}_3)_5]\text{Cl}$	Pentaamminecarbonatocobalt(III) chloride
12.	$[\text{Ir}(\text{en})_2(\text{NH}_3)_2]\text{Cl}_3$	Diammine bis(1,2-ethanediamine)iridium(III) chloride
13.	$[\text{CoCl}(\text{NH}_3)_4\text{NO}_2]\text{ClO}_4$	Tetraamminechloridonitritocobalt(III) perchlorate
14.	$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	Diamminesilver(I) chloride
15.	$[\text{CoBrCl}(\text{en})(\text{ONO})_2]^{\oplus}$	Bromidochlorido(1,2-ethanediamine)dinitrito-O-cobalt (III) ion
16.	$[\text{Co}(\text{en})(\text{NH}_3)_2\text{BrCl}]\text{NO}_3$	Diaminebromidochlorido(ethylenediamine)cobalt(III)nitrate
17.	$[\text{CoCl}(\text{en})_2\text{ONO}]^{\oplus}$	Chloridobis(ethylenediamine) nitrito-O-cobalt(III) ion.
18.	$[\text{Co}(\text{NH}_2)_2(\text{NH}_3)_4]\text{OC}_2\text{H}_5$	Diamidotetraamminecobalt(III) ethoxide
19.	$[\text{CoN}_3(\text{NH}_3)_5]\text{SO}_4$	Pentaammineazidocobalt(III) sulphate
20.	$[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$	Tris(1,2-ethanediamine)cobalt(III) sulphate
21.	$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	Hexaaquachromium(III) chloride
22.	$[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$	Pentaamminedinitrogenruthenium(II) chloride
23.	$[\text{Co}(\text{NCS})(\text{NH}_3)_5]\text{Cl}_2$	Pentaammine-thiocyanato-N-cobalt(III) chloride
24.	$[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{SO}_4$	Pentaamminenitrito-O-cobalt(III) sulphate
b.	Complex anions	IUPAC name
25.	$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$	Potassium trioxalatoferrate(III)
26.	$\text{K}_2[\text{Co}(\text{CN})_5(\text{NO})]$	Potassium pentacyanonitrosylcobaltate(III)
27.	$\text{K}[\text{PtCl}_3(\text{NH}_3)]$	Potassium amminetrichloridoplatinate(II)
28.	$\text{Na}_2[\text{CrOF}_4]$	Sodium tetrafluoridooxochromate (IV)
29.	$\text{Na}_2[\text{SiF}_6]$	Sodium hexafluoridosilicate(IV)
30.	$[\text{Hg}[\text{Co}(\text{SCN})_4]$	Mercuric tetrathiocyanatocobaltate(II)
31.	$\text{K}_4[\text{Ni}(\text{CN})_4]$	Potassium tetracyanonickelate(0)
32.	Dextro $\text{K}_3[\text{Ir}(\text{C}_2\text{O}_4)_3]$	Potassium d-trioxalatoiridate(III)
33.	$\text{Li}[\text{AlH}_4]$	Lithium tetrahydridoaluminate(III)
34.	$(\text{NH}_4)_2[\text{Pt}(\text{SCN})_6]$	Ammonium hexathiocyanatoplatinate (IV)
35.	$\text{K}_3[\text{Co}(\text{NO}_2)_6]$	Potassium hexanitritocobaltate(III)
36.	$\text{K}_3[\text{Co}(\text{NO}_2)_6]$	Potassium hexanitritocobaltate(III)
37.	$(\text{NH}_4)[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$	Ammonium diamminetetrathiocyanato-N-chromate(III)
38.	$[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_2(\text{CO}_3)]^{\ominus}$	Triaquacarbonatodichloridocobaltate(III) ion
39.	$[\text{Cr}(\text{NEt}_2)_4]^{\ominus}$	Tetrakisdiethylamidochromate(III) ion
40.	$\text{K}_2[\text{OsCl}_5\text{N}]$	Potassium pentachloridonitridoosmate(VI)
41.	$\text{K}_3[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(III)
42.	$\text{K}_4[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(II)
43.	$\text{Na}[\text{B}(\text{NO}_3)_4]$	Sodium tetranitratoborate (IV)

14. $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$	Sodium bis(thiosulphato)argentate(I)
15. $\text{K}[\text{B}(\text{C}_6\text{H}_5)_4]$	Potassium tetra(phenyl)borate(III)
16. $\text{K}[\text{SbCl}_5\text{C}_6\text{H}_5]$	Potassium pentachlorido(phenyl)antimonate(V)
17. $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$	Potassium trichlorido(ethylene) platinate(II)
18. $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NO}]$	Sodium pentacyanonitrosylferrate(II)
19. $\text{K}_3[\text{Fe}(\text{CN})_5\text{CO}]$	Potassium carbonylpentacyanoferrate(II)
20. $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	Sodium hexanitrito-N-cobaltate(III)
21. $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$	Potassium trioxalatoaluminate(III)
22. $\text{Ca}_2[\text{Fe}(\text{CN})_6]$	Calcium hexacyanoferrate(II)
23. $\text{Na}[\text{Co}(\text{CO})_4]$	Sodium tetracarbonylcobaltate(-I)
24. $(\text{NH}_4)_3[\text{Cr}(\text{NCS})_6]$	Ammonium hexathiocyanato-N-chromate(III)
25. $\text{K}_3[\text{Cr}(\text{CN})_6]$	Potassium hexacyanochromate(III)

Note: For CN^\ominus either cyano or cyanido may be written.

c. Neutral complexes	IUPAC name
56. $[\text{Ni}(\text{CO})_4]$	Tetracarbonylnickel(0)
57. $[\text{Co}(\text{NO})_3(\text{NH}_3)_3]$	Triamminetrinitrito-N-cobalt(III)
58. $[\text{PtCl}_2(\text{NH}_3)_2]$	Diamminedichloridoplatinum(II)
59. $[\text{Cr}(\text{PPh}_3)(\text{CO})_5]$	Pentacarbonyltriphenylphosphinechromium(0)
60. $[\text{Ni}(\text{dmg})_2]$	Bis(dimethylglyoximate)nickel(II)
61. $[\text{Mn}_3(\text{CO})_2]$	Dodecacarbonyltrimanganese(0)
62. $[\text{Cr}(\text{NH}_3)(\text{NO}_2)_3]$	Triamminetrinitritochromium(III)
63. $[\text{CuCl}_2(\text{CH}_3\text{CH}_2)_2]$	Dichloridobis(methylamine)copper(II)
64. $\text{cis-}[\text{PtCl}_2(\text{PEt}_3)_2]$	cis-dichloridobis(triethylphosphine)platinum(II)
65. $[\text{Cu}(\text{gly})_2]$	Diglycinatocopper(II)
66. $[\text{CuCl}_2(\text{O}=\text{C}(\text{NH}_2))_2]\text{Cl}_2$	Dichloridobis(urea)copper(II)

d. Complexes containing cationic and anionic ions	IUPAC name
67. $[\text{PtCl}_2(\text{NH}_3)_4][\text{PtCl}_4]$	Tetraamminedichloridoplatinum(IV) tetrachloridoplatinate(II)
68. $[\text{CoCl}_2(\text{NH}_3)_4]_3[\text{Cr}(\text{CN})_6]$	Tetraamminedichloridocobalt(III) hexacyanidochromate(III)
69. $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$	Tetraammineplatinum(II) tetrachloridoplatinate(II)
70. $[\text{Cr}(\text{en})_3][\text{FeCl}_4]_3$	Tris(1,2-ethanediamine) chromium(III) tetra-chloridoferrate(III)
71. $[\text{Pt}(\text{py})_2][\text{PtCl}_4]$	Tetrakis(pyridine)platinum(II) tetrachloridoplatinate(II)

e. Bridge complexes	IUPAC name
72. $[(\text{NH}_3)_5\text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_5]\text{Cl}_5$	μ -Hydroxobis(pentaamminechromium(III) chloride
73. $\left[\begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ (\text{H}_2\text{O})_4\text{Fe} \quad \text{Fe}(\text{H}_2\text{O})_4 \\ \diagdown \quad \diagup \\ \text{OH} \end{array} \right] (\text{SO}_4)_2$	Di- μ -hydroxobis(tetraaquairon(III) sulphate
74. $\left[\begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ (\text{NH}_3)_4\text{Co} \quad \text{Co}(\text{NH}_3)_4 \\ \diagdown \quad \diagup \\ \text{NO}_2 \end{array} \right] (\text{NO}_3)_4$	μ -Amido- μ -nitritobis(tetraamminecobalt(III)) nitrate
75. $\text{K}_2 \left[\text{Ni} \left(\begin{array}{c} \text{O}=\text{C}-\text{S} \\ \\ \text{O}=\text{C}-\text{S} \end{array} \right)_2 \right]$	Potassium bis(thiooxalato-O-O')nickelate(II)
76. $\left[\begin{array}{c} \text{S} \quad \text{O} \quad \text{S} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \end{array} \text{Pt} \right]^{2-}$	Thiosulphato-O-O'-thiosulphato-O-S-platinate(II) ion

77.		Tris-μ-carbonylbis(tricarbonyliron(0))
78.		trans-Di-μ-chloridobis(chloridotriphenylphosphineplatinum(II))
79.	$[(\text{CO})_5\text{Mn}-\text{Mn}(\text{CO})_5]$	Bis(pentacarbonylmanganese(0))
80.		μ-Peroxo-μ-superoxobis(tetraamminechromium(III)) bromide
81.		Di-μ-peroxobis(tetraamminechromium(III)) perchlorate
82.		Di-μ-superoxobis(tetraaquacobalt(III)) perbromate

Table 7.10 Names and structures of some abbreviations used in complexes

S.No.	Abbreviations	Name and structure
1.	acac [⊖]	Acetyl acetonato ion
2.	acacH	Acetylacetone
3.	am	Ammonia (NH ₃)
4.	aq	Aqua (H ₂ O)
5.	big	Biguanido ion
6.	big H	Biguanide
7.	dien	Diethylenetriamine (NH ₂ -(CH ₂) ₂ -NH-(CH ₂) ₂ -NH ₂)
8.	DMG [⊖]	Dimethylglyoximatio ion
9.	DMGH	Dimethylglyoxime
10.	EDTA ⁴⁻	Ethylenediaminetetraacetatoion
11.	EDTAH ₄	Ethylenediaminetetraaceticacid
12.	en	Ethylenediamine
13.	eten	N-ethylethylenediamine [H ₂ N-(CH ₂) ₂ -NH-C ₂ H ₅]
14.	gly [⊖]	Glycinato ion (NH ₂ -CH ₂ -COO [⊖])
15.	glyH	Glycine
16.	IDA ²⁻	Imidodiacetato ion
17.	IDA H ₂	Imidodiacetic acid
18.	OX ²⁻	Oxalato ion [[⊖] OOC-COO [⊖]]

19.	OXH_2	Oxalic acid
20.	tetraen	Tetraethylenepentamine
21.	trien	Triethylenetetramine
22.	ph	Ortho-phenthroline
23.	pn	1, 2-Diaminepropane
24.	tn	1, 3-Diaminepropane

Table 7.11 Formulae of the coordination compounds

S.No.	Name	Formula
1.	Sodium pentacyanonitrosylferrate(III)	$\text{Na}_2[\text{Fe}^{+3}(\text{CN}^{-5})_5\text{NO}^0]^{-2}$
2.	Hexakis(ethanenitrile)iron(II) chloride	$[\text{Fe}(\text{CH}_3\text{CN})_6]\text{Cl}_2$
3.	Pentaamminedinitrogenruthenium(II) chloride	$[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2$
4.	Tetraethylammonium diamminetetrathiocyanato-N-chromate(III)	$(\text{NEt})_4[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$
5.	Triamminecarbonatodichlorido cobaltate(III) ion	$[\text{CoCl}_2(\text{CO}_3)(\text{NH}_3)_3]^\ominus$
6.	Ammonium hexathiocyanato-S-platinate(IV)	$(\text{NH}_4)_2[\text{Pt}(\text{SCN})_6]$
7.	trans-diamminedichloridoplatinum(II)	$\begin{array}{c} \text{H}_3\text{N} \quad \text{Cl} \\ \quad \diagdown \quad \diagup \\ \quad \text{Pt} \\ \quad \diagup \quad \diagdown \\ \text{Cl} \quad \text{NH}_3 \end{array}$
8.	Ammonium tetraamminediisothiocyanato chromate(III)	$(\text{NH}_4)_2[\text{Cr}(\text{NH}_3)_4(\text{NCS})_2]$
9.	Tetraamminechloridothiocyanato-N-cobalt(III)	$[\text{CoCl}(\text{NH}_3)_4(\text{NCS})]\text{NO}_3$
10.	Tetrachlorido(1, 2-ethanediamine) platinum(IV)	$[\text{PtCl}_4(\text{en})]$
11.	Sodium diamminetetracyanochromate(III)	$\text{Na}[(\text{Cr}(\text{NH}_3)_2(\text{CN})_4)]$
12.	Sodium ethylenediaminetetraacetato nickelate(II)	$\text{Na}_2[\text{Ni}(\text{edta})]$
13.	Potassium tetracyanonickelate(0)	$\text{K}_4[\text{Ni}(\text{CN})_4]$
14.	Amminebromidochloridomethylamine platinum(II)	$[\text{PtBrCl}(\text{NH}_3)(\text{CH}_3\text{NH}_2)]$
15.	cis-tetraamminedichloridocobalt(III) chloride	$\left[\begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{Co} \\ \diagdown \quad \diagup \\ \text{H}_3\text{N} \quad \text{NH}_3 \\ \quad \quad \text{NH}_3 \end{array} \right] \text{Cl}$
16.	Tetraaquadichloridochromium(III) nitrate	$[\text{CrCl}_2(\text{OH}_2)_4]\text{NO}_3$
17.	Ammonium aquapentafluoronickelate(IV)	$(\text{NH}_4)_2[\text{NiF}_5(\text{H}_2\text{O})]$
18.	Bromidodichloridodidoplatinate(IV)	$[\text{PtBrCl}_2\text{I}]$
19.	Magnesium hexacyanoferrate(II)	$\text{Mg}_2[\text{Fe}(\text{CN})_6]$
20.	Potassium tetraoxoferrate (IV)	$\text{K}_4[\text{Fe}(\text{O})_4]$
21.	Potassium tetrazidocobaltate(II)	$\text{K}_2[\text{Co}(\text{N}_3)_4]$
22.	Dichloridobis (triphenylphosphine) nickel(II)	$[\text{NiCl}_2(\text{PPh}_3)_2]$
23.	Chloridocarbonylbis(triphenylphosphine) iridium(I)	$[\text{IrClCO}(\text{PPh}_3)_2]$
24.	Hexaamminecobalt(III) diamminetetrachlorido chromate (III)	$[\text{Co}(\text{NH}_3)_6][\text{CrCl}_4(\text{NH}_3)_2]$
25.	Hexaamminenickel(II) hexanitritocobaltate(III)	$[\text{Ni}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$
26.	Tetraamminedibromidocobalt(II) tetrachloridozincate(II)	$[\text{CoBr}_2(\text{NH}_3)_4][\text{ZnCl}_4]$
27.	Tetramminesulphatocobalt(III) nitrate	$[\text{Co}(\text{NH}_3)_4(\text{SO}_4)]\text{NO}_3$

28.	Triamminechloridocyanonitritocobalt(III)	$[\text{CoCl}(\text{CN})(\text{NH}_3)_3(\text{NO}_2)]$
29.	Tetrathiocyanato-N-zinc(II) ion	$[\text{Zn}(\text{NCS})_4]^{2+}$
30.	Tetrathiocyanato-S-cadmium(II) ion	$[\text{Cd}(\text{SCN})_4]^{2+}$
31.	Lithium tetrahydridoaluminate(III)	$\text{Li}[\text{AlH}_4]$
32.	Potassium amminetricyanooxoperoxochromate (V)	$\text{K}_2^{+2}[\text{Cr}^{+5}(\text{CN}^-)_3\text{O}^{2-}(\text{O}_2)^{2-}\text{NH}_3]^{-2}$
33.	Potassium amminetricyanooxosuperoxochromate (IV)	$\text{K}_2^{+2}[\text{Cr}^{+4}(\text{CN}^-)_3\text{O}^{2-}(\text{O}_2)^{-1}\text{NH}_3]^{-2}$
34.	Calcium oxoperoxosuperoxotriaquachromate (III)	$\text{Ca}^{+2}[\text{Cr}^{+3}(\text{H}_2\text{O}^0)_3\text{O}^{2-}(\text{O}_2)^{-2}(\text{O}_2)^{-1}]^{-2}$
35.	Potassium oxodisuperoxotriaquachromate (III)	$\text{K}^{+1}[\text{Cr}^{+3}(\text{H}_2\text{O}^0)_3\text{O}^{2-}(\text{O}_2)^{-1 \times 2}]^{-1}$
36.	Aluminium oxodisuperoxo triqua chromate (III)	$\text{Al}^{+3}[\text{Cr}^{+3}(\text{H}_2\text{O}^0)_3\text{O}^{2-}(\text{O}_2)^{-2 \times 2}]^{-3}$
37.	Bis (cyclopentadienyl) iron (II)	$[\text{Fe}(\text{C}_5\text{H}_5)_2]$
38.	Dibenzene chromium (0)	$[\text{Cr}(\text{C}_6\text{H}_6)_2]$
39.	Ammonium heptafluoridozirconate(IV)	$(\text{NH}_4)_3 [\text{ZrF}_7]$
40.	Tetraaquadibromidochromium(III) chloride	$[\text{Cr}(\text{H}_2\text{O})_4\text{Br}_2]\text{Cl}$

ILLUSTRATION 7.6

Write the formula for the following coordination compounds.

- I. a. Tetraamineaquachlorido cobalt (III) chloride
 b. Potassium tetrahydroxozincate (II)
 c. Potassium trioxalatoaluminate (III)
 d. Dichloridobis (ethane-1, 2-diamine)cobalt(III) ion
 e. Tetracarbonylnickel(0)
- II. Write the IUPAC names of the following coordination compounds.
 a. $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$
 b. $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
 c. $[\text{CoCl}_2(\text{en})_2]\text{Cl}$
 d. $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$
 e. $\text{Hg}[\text{Co}(\text{SCN})_4]$

- Sol.** I. a. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$
 b. $\text{K}_2[\text{Zn}(\text{OH})_4]$ c. $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$
 d. $[\text{CoCl}_2(\text{en})_2]^{\oplus}$ e. $[\text{Ni}(\text{CO})_4]$
- II. a. Diamminechloridonitrito-N-platinum(II)
 b. Potassium trioxalatochromate(III)
 c. Dichloridobis (ethane-1, 2-diamine) cobalt(III) chloride
 d. Pentaamminecarbonatocobalt(III) chloride
 e. Mercury tetrathiocyanatocobaltate(III)

ILLUSTRATION 7.7

Write the formula for the following coordination compounds.

- a. Tetrahydroxozincate(II) ion
 b. Pentaquachloridochromium(II) chloride
 c. Tetrabromidocuprate(II) ion
 d. Pentacarbonyl iron(0)

- e. Potassium tetracyanocuprate(II)
 f. Tetraamminediaquanickel(II) sulphate
 g. Tetraaquadichloridoiron (III) ion
 h. Potassium trioxalatochromate (III)
 i. Pentachloridoazidoosmium(IV) ion
 j. Triaquachloridoplatinum(II) bromide.

- Sol.** a. $[\text{Zn}(\text{OH})_4]^{2-}$ b. $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}^+$
 c. $[\text{CuBr}_4]^{2-}$ d. $[\text{Fe}(\text{CO})_5]$
 e. $\text{K}_2[\text{Cu}(\text{CN})_4]$ f. $[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4](\text{SO}_4)^{-2}$
 g. $[\text{FeCl}_2(\text{H}_2\text{O})_4]^{\oplus}$ h. $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]^{-3}$
 i. $[\text{OsCl}_5(\text{N}_3)]^{-1}$ j. $[\text{PtCl}(\text{H}_2\text{O})_5]\text{Br}^{-1}$

ILLUSTRATION 7.8

Name the following complex ions:

- a. $[\text{PdBr}_4]^{2-}$ b. $[\text{CuCl}_2]^{\ominus}$
 c. $[\text{Au}(\text{CN})_4]^{\ominus}$ d. $[\text{AlF}_6]^{3-}$
 e. $[\text{Cr}(\text{NH}_3)_6]^{3+}$ f. $[\text{Zn}(\text{NH}_3)_4]^{2+}$
 g. $[\text{Fe}(\text{CN})_6]^{3-}$

- Sol.** a. Tetrabromidopalladate(II) ion
 b. Dichloridocuprate(I) ion
 c. Tetracyanoaurate(III) ion
 d. Hexafluoroaluminate(III) ion
 e. Hexaamminechromium(III) ion
 f. Tetraamminezincate(II) ion
 g. Hexacyanoferrate(III) ion

7.6 WERNER'S COORDINATION THEORY

Alfred Werner is known as father of coordination chemistry. Werner's coordination theory (in 1893) was the first attempt to explain the bonding in the coordination complexes. This theory and his painstaking work over the next 20 years won Alfred Werner, the Nobel Prize in chemistry in 1913.

The chief methods available to Werner for the investigation of complexes were the study of chemical reactivity, electrical conductivity and isomerism. The following example, taken from his work illustrate their applications by the action of oxidising agents on solution of cobalt (II) chloride in the presence of ammonia the following compounds are formed.

S. No.	Compound	No. of chloride ions precipitated by AgNO_3	Molar conductivity	Cryoscopic studies
1.	$\text{CoCl}_3 \cdot 6\text{NH}_3$ Leuticobaltic chloride (yellow)	3	6 charges	4 particles
2.	$\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ Rosecobaltic chloride (Red)	3	6 charges	4 particles
3.	$\text{CoCl}_3 \cdot 5\text{NH}_3$ Purplecobaltic chloride (Purple)	2	4 charges	3 particles
4.	$\text{CoCl}_3 \cdot 4\text{NH}_3$ Violetcobaltic chloride (Violet)	1	2 charges	2 particles
5.	$\text{CoCl}_3 \cdot 4\text{NH}_3$ Parasecobaltic chloride (Green)	1	2 charges	2 particles

7.6.1 MAIN POSTULATES OF WERNER'S THEORY

To explain the above observations, Werner proposed Werner's coordination theory. Its postulates are:

1. A metal possesses two types of valencies:
 - a. Primary or ionisable valency (.....)
 - b. Secondary or non-ionisable valency (—)
2. Characteristics of primary or ionisable valency:
 - i. It corresponds to the oxidation state of the metal atom/ion or charge carried by the metal ion in the compound.
 - ii. Primary valence of the metal ion is neutralised and satisfied by negative ion such as Cl^- , SO_4^{2-} etc.
 - iii. The attachment of metal ion with the negative ligand is shown by dotted lines (---).
3. Characteristics of secondary or non-ionisable valency:
 - i. This corresponds to the coordination number of the metal atom or ion.
 - ii. Secondary valencies may be satisfied by either negative ions or neutral molecules.

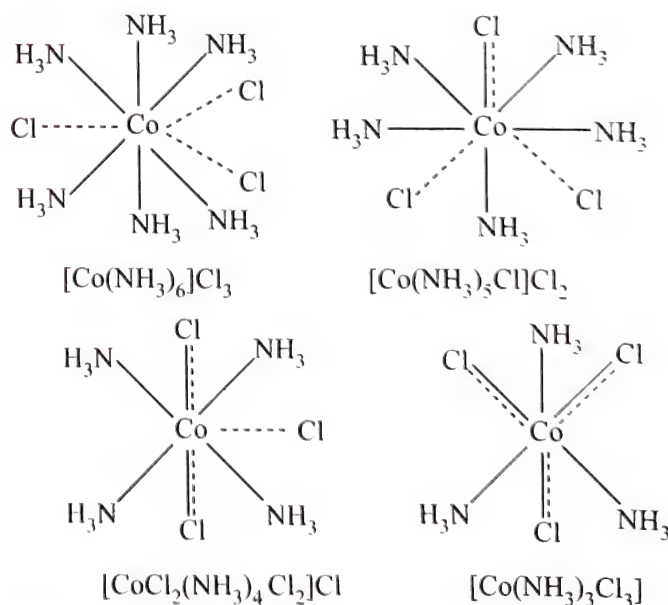
- iii. Ligands are directly attached to the metal atom/ion by secondary valency and are shown by thick line (—).
- iv. In modern terms, while writing the structure of a complex species satisfying the secondary valence and metal are written inside the coordination sphere (represented by []).
- v. Secondary valencies are directional in character, since the species satisfying the secondary valency (i.e. ligands) are directed towards the fixed position in space, which gives rise to characteristic spatial arrangement corresponding to different coordination numbers. Such spatial arrangements are called **coordination polyhedra**.

Werner observed that every element must satisfy all its primary and secondary valencies.

In order to meet this requirement the negative ion may have a dual behaviour, i.e., in satisfying the primary valency and in satisfying the secondary valency. Further the ligands which satisfying the secondary valencies must point out in definite directions in space whereas the primary valencies are non-directional in nature. Thus the presence of secondary valencies attribute to the isomerism in inorganic complexes, i.e., stereoisomerism.

Thus on the basis of Werner theory $\text{CoCl}_3 \cdot 6\text{NH}_3$ is called hexammine cobalt (III) chloride because there are six ammonia ligands and the cobalt is in the +3 oxidation state, i.e. cobalt has three primary valencies and six secondary valencies.

Similarly, other complexes of cobalt and ammonia such as $\text{CoCl}_3 \cdot 5\text{NH}_3$, $\text{CoCl}_3 \cdot 4\text{NH}_3$ and $\text{CoCl}_3 \cdot 3\text{NH}_3$ can be represented as follows.



It is clear from the above formulae that complex compound (as given by Werner), has one characteristic feature, i.e., some of the negative ligands such as chlorine has to perform two functions in satisfying both the primary and secondary valencies and is shown to be attached to the metal ion by dotted and thick lines. Such valencies which perform a dual role are not ionised.

Thus the above compounds will have varying number of ionisable chlorine atoms which is represented as below:

Compound	No. of ionisable chlorine atoms
$\text{CoCl}_3 \cdot 6\text{NH}_3$	3
$\text{CoCl}_3 \cdot 5\text{NH}_3$	2
$\text{CoCl}_3 \cdot 4\text{NH}_3$	1
$\text{CoCl}_3 \cdot 3\text{NH}_3$	Nil

In modern terms the complex ions are shown in square brackets with ionisable ligands outside the coordination sphere. The primary valencies are ionic bonds whereas secondary valencies are coordinate bonds. Thus the above complex can be rewritten in modern terms as below:

Werner formula	Modern formula	Cation	Anion	Total no. of ions
$\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+}$	3Cl^-	4
$\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$	2Cl^-	3
$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$	Cl^-	2
$\text{CoCl}_3 \cdot 3\text{NH}_3$	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	Non-electrolyte	—	zero

7.6.2 FAILURE OF WERNER'S THEORY

Werner was the first to describe the bonding features in coordination compounds. But his theory could not answer basic questions like:

- Why only certain elements possess the remarkable property of forming coordination compounds?
- Why the bonds in coordination compounds have direction properties?
- Why coordination compounds have characteristic magnetic and optical properties?

Many approaches have been put forth to explain the nature of bonding in coordination compounds viz. valence theory (VBT), crystal field theory (CFT), ligand field theory (LFT) and molecular orbital theory (MOT). However, we shall be restricting ourselves to VBT and CFT only.

ILLUSTRATION 7.9

From the experimental facts given below determine the correct structure of solid $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. Solution containing 0.2665 g of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was passed through cation exchange resin in acid form. The acid liberated was found to react completely with 30 mL of 0.10 M NaOH. (Molecular mass of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ = 266.5)

- a. 0 b. 1 c. 2 d. 3

Sol. d. Moles of compound = $\frac{0.2665}{266.5} = 10^{-3}$ moles

$$\text{Moles of NaOH} = \frac{30 \text{ mL} \times 0.10 \text{ M}}{1000 \text{ mL}} = 3 \times 10^{-3}$$

$$\text{Moles of NaOH} = \text{Moles of HCl} = 3 \times 10^{-3}$$

Let 1 mole of compound contains n moles of replaceable Cl^- ions.

$\therefore 10^{-3}$ moles of compound contains = $n \times 10^{-3}$ moles of Cl^- ions.

$$\therefore n \times 10^{-3} = 3 \times 10^{-3}$$

Therefore, there are 3 moles of replaceable Cl^- in the compound. So, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is represented as $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$.

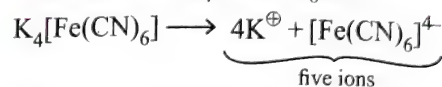
ILLUSTRATION 7.10

Which of the following complexes (in solution) will have greater value of molar conductivity? Explain giving reason.

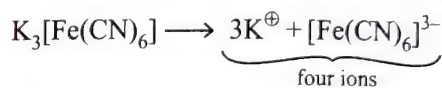
- $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{K}_3[\text{Fe}(\text{CN})_6]$
- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$

Sol.

- a. On ionisation, $\text{K}_4[\text{Fe}(\text{CN})_6]$ gives

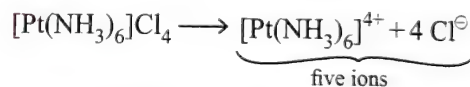


Whereas $\text{K}_3[\text{Fe}(\text{CN})_6]$ on ionisation gives



Since $\text{K}_4[\text{Fe}(\text{CN})_6]$ gives more number of ions (i.e. five ions) as compared to $\text{K}_3[\text{Fe}(\text{CN})_6]$, (i.e. four ions) on ionisation, $\text{K}_4[\text{Fe}(\text{CN})_6]$ will have greater value of molar conductivity.

- b. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is a non-electrolyte, it does not ionise in solution whereas $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ ionises to give



Hence $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ will have greater molar conductivity as compared to $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

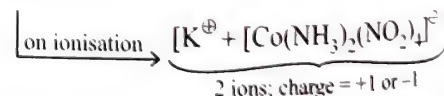
ILLUSTRATION 7.11

Arrange the following in order of increasing molar conductivity:

- $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$
- $[\text{Cr}(\text{NH}_3)_3(\text{NO}_2)_3]$
- $[\text{Cr}(\text{NH}_3)_5(\text{NO}_2)]_3 [\text{Co}(\text{NO}_2)_6]_2$
- $\text{Mg}[\text{Co}(\text{NH}_3)(\text{NO}_2)_5]$

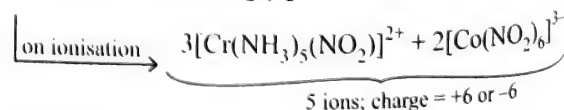
Sol. In aqueous solution

- a. $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$

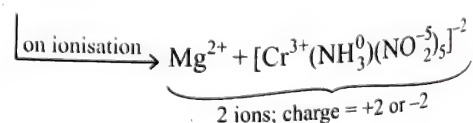


- b. $[\text{Cr}(\text{NH}_3)_3(\text{NO}_2)_3]$ being non-electrolyte, does not ionise.

- c. $[\text{Cr}(\text{NH}_3)_5(\text{NO}_2)]_3 [\text{Co}(\text{NO}_2)_6]_2$



- d. $\text{Mg}[\text{Cr}(\text{NH}_3)(\text{NO}_2)_5]$



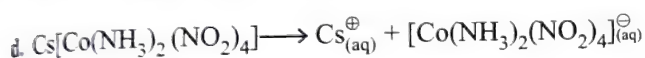
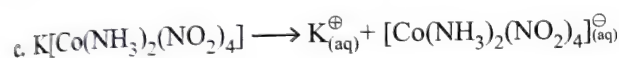
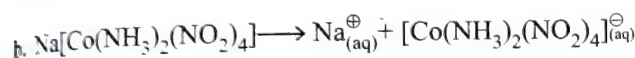
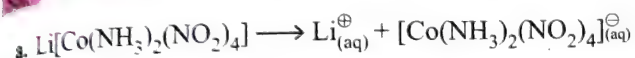
Greater the number of ions and greater the total (positive or negative) charge produced after ionisation, greater is the value of molar conductivity. Hence, increasing order of molar conductivity is $b < a < d < c$.

ILLUSTRATION 7.12

Arrange the following in order of decreasing molar conductivity in aqueous solution:

- $\text{Li}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$
- $\text{Na}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$
- $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$
- $\text{Cs}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$

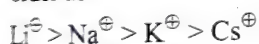
The above mentioned complexes ionises as follows:



In all the cases, the number of ionic species produced are same (two in each case), the number of charges produced are same (+1 or -1). Molar conductivity depends directly on the mobility or movement of species produced on ionisation.

Mobility of ions \propto charge density.

Since the charge density (ionic charge/ionic radius) decreases and hence the mobilities of ions should be in the order as:



But in aqueous solution, the above order of mobilities is reversed, because hydration \propto charge density \propto mobilities. So Li^+ ion is extensively hydrated than Cs^+ ion and hence the mobilities and conductance of the above compounds is in the order $d > c > b > a$.

7.7 SIDGWICK'S ELECTRONIC CONCEPT OF COORDINATE BOND

In 1927, Sidgwick introduced the concept of coordinate bond, which is also sometimes called polar or dative bond. According to Sidgwick, a ligand donates an electron pair to the central metal ion and thus a coordinate bond is formed, which is designated as $\text{L} \rightarrow \text{M}$. This concept is based on the fact that all the ligands contain at least one lone pair of electrons.

7.7.1 SIDGWICK'S EFFECTIVE ATOMIC NUMBER (EAN) RULE

On the basis of his concept of coordinate bond, Sidgwick suggested that central metal ion will continue accepting electron pairs from the ligands till the total number of electron surrounding the metal ion including those donated by the ligands is equal to that of next noble gas. The total number of electrons is called **Effective Atomic Number** and the rule is known as **Effective Atomic Number (EAN) rule**.

Effective atomic number of central atom/ion in the complex can be calculated as follows:

$$\text{EAN} = Z - X + Y$$

Z = Atomic number of central atom/ion

X = Oxidation state of central atom/ion

Y = No. of electrons gained by $\text{L} \rightarrow \text{M}$ coordination

Table 7.12 Complexes whose central atom/ion obeys EAN rule

Complex	Central atom	Atomic Number (Z)	Oxidation state of central atom (X)	Electrons gained by coordination (Y)	EAN (= Z - X + Y)	Atomic number of next higher noble gas
$[\text{Fe}(\text{CN})_6]^{4-}$	Fe	26	+2	$2 \times 6 = 12$	$26 - 2 + 12 = 36$	Kr = 36
$[\text{Cu}(\text{CN})_4]^{3-}$	Cu	29	+1	$2 \times 4 = 8$	$29 - 1 + 8 = 36$	Kr = 36
$[\text{Pd}(\text{NH}_3)_6]^{4+}$	Pd	46	+4	$2 \times 6 = 12$	$46 - 4 + 12 = 54$	Xe = 54
$[\text{PdCl}_4]^{2-}$	Pd	46	+2	$2 \times 4 = 8$	$46 - 2 + 8 = 54$	Xe = 54
$[\text{Pt}(\text{NH}_3)_4]^{2+}$	Pt	78	+2	$2 \times 4 = 8$	$78 - 2 + 8 = 84$	Rn = 86
$[\text{Cr}(\text{CO})_6]$	Cr	24	0	$2 \times 6 = 12$	$24 - 0 + 12 = 36$	Kr = 36
$[\text{Fe}(\text{CO})_5]$	Fe	26	0	$2 \times 5 = 10$	$26 - 0 + 10 = 36$	Kr = 36
$[\text{Ni}(\text{CO})_4]$	Ni	28	0	$2 \times 4 = 8$	$28 - 0 + 8 = 36$	Kr = 36

EAN rule has some usefulness, that is, it predicts the number of ligands in many complexes. It has, however, only of qualitative significance, because there are many other complexes which are known to be very stable, but do not obey EAN rule, as shown in Table 7.13.

Table 7.13 Complex whose central atom does not obeys EAN rule

Complex	Central atom	Atomic number (Z)	Oxidation state (X)	Electrons gained by coordination (Y)	EAN (= Z - X + Y)
$[\text{Fe}(\text{CN})_6]^{3-}$	Fe	26	+3	$2 \times 6 = 12$	$26 - 3 + 12 = 35$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	Cr	24	+3	$2 \times 6 = 12$	$24 - 3 + 12 = 33$
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	Ni	28	+2	$2 \times 6 = 12$	$28 - 2 + 12 = 38$
$[\text{Ni}(\text{en})_3]^{2+}$	Ni	28	+2	$*2 \times 3 \times 2 = 12$	$28 - 2 + 12 = 38$
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	Mn	25	+2	$2 \times 6 = 12$	$25 - 2 + 12 = 35$
$[\text{Co}(\text{CN})_6]^{4-}$	Co	27	+2	$2 \times 6 = 12$	$27 - 2 + 12 = 37$
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	Cu	29	+2	$2 \times 4 = 8$	$29 - 2 + 8 = 35$
$[\text{Ni}(\text{CN})_4]^{2-}$	Ni	28	+2	$2 \times 4 = 8$	$28 - 2 + 8 = 34$

*Note: (en) is bidentate ligand.

7.7.2 APPLICATIONS OF EAN RULE

1. It predicts the number of unpaired electrons in the complex and hence magnetic moment.
2. It predicts the molecular formula of simple carbonyl.

ILLUSTRATION 7.13

Calculate the EAN of the underlined atoms in the following complexes.

- a. $[\text{Ca}(\text{edta})]^{2-}$
- b. $[\text{Ni}(\text{py})(\text{en})(\text{NH}_3)_3]^{2+}$

Sol.

- a. $[\text{Ca}(\text{edta})]^{2-}$

(Z of Ca = 20)

Let oxidation state of Ca be x,

$$\therefore x + 1 \times (-4) = -2$$

$$\Rightarrow x = +2$$

Coordination number of (edta) = 6.

(\because edta⁴⁻ is hexadentate ligand)

$$\therefore \text{EAN of Ca} = (20 - 2) + 2 \times 6 = 30$$

So, EAN rule is not valid.

- b. $[\text{Ni}(\text{py})(\text{en})(\text{NH}_3)_3]^{2+}$

Ni (Z = 28);

Let oxidation state of Ni be x,

$$\therefore x + 0 + 0 + 3 \times 0 = 2$$

$$\Rightarrow x = +2$$

[Pyridine, (py); and ammonia, (NH₃) are monodentate ligand whereas ethylenediamine (en) is bidentate ligand]

So, EAN of Ni = $(28 - 2) + 2 + 2 + 2 \times 3 = 38$

So, EAN rule is not valid.

ILLUSTRATION 7.14

Deduce the value of x in the following compounds.

- a. $[\text{Mo}(\text{CO})_x]$
- b. $[\text{Co}_2(\text{CO})_x]$
- c. $\text{H}_x\text{Cr}(\text{CO})_5$
- d. $\text{H}_x\text{Co}(\text{CO})_4$
- e. $[\text{Fe}(\text{C}_5\text{H}_5)_2]$
- f. $[\text{Cr}(\text{C}_6\text{H}_6)_2]$

Sol.

- a. In $[\text{Mo}(\text{CO})_x]$, EAN of Mo = 54

Z of Mo = 42

Oxidation state of Mo is zero

No. of electrons donated by x CO groups = 2x

EAN of Mo in $[\text{Mo}(\text{CO})_x]$

$$42 - 0 + 2x = 54$$

$$\therefore x = \frac{54 - 42}{2} = 6$$

$$x = 6$$

Formula is $[\text{Mo}(\text{CO})_6]$.

- b. $[\text{Co}_2(\text{CO})_x]$

Atomic number (Z) of Co = 27

Oxidation state of Co = 0

In $[\text{Co}_2(\text{CO})_x]$, i.e. one electron is shared with other Co atom due to Co-Co bond, which means contribution coming because of Co-Co bond is 1.

For EAN of each Co = 36,

$$27 - 0 + 1 + \frac{2x}{2} = 36$$

$$\Rightarrow x = 8$$

Formula is $\text{Co}_2(\text{CO})_8$

- c. $\text{H}_x\text{Cr}(\text{CO})_5$

Atomic number (Z) of Cr = 24

Electrons gained by 5 CO groups = $2 \times 5 = 10$

$$\text{EAN of Cr} = 36 = 24 + 10 + x$$

$$\Rightarrow x = 36 - 24 - 10 = 2$$

i.e., formula is $\text{H}_2\text{Cr}(\text{CO})_5$.

- d. $\text{H}_x\text{Co}(\text{CO})_4$

Atomic number (Z) of Co = 27

Electrons gained by Co due to 4 CO groups = $2 \times 4 = 8$

$$\text{EAN of Co} = 36 = 27 + 8 + x$$

$$\Rightarrow x = 36 - 27 - 8 = 1$$

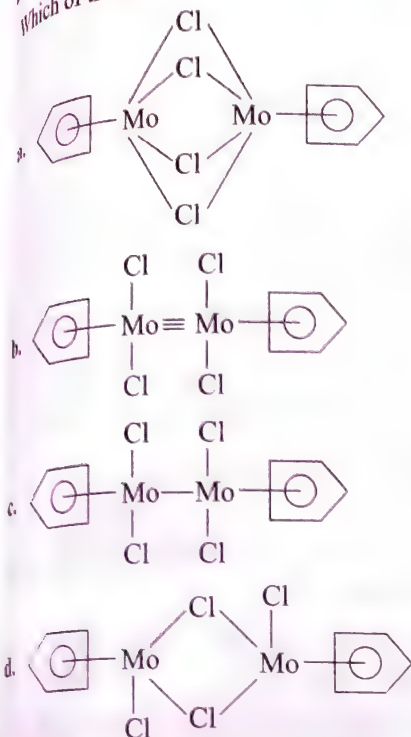
i.e. formula is $\text{HCo}(\text{CO})_4$.

- e. EAN = 36 f. EAN = 36

Refer to Section 7.16.1(b), Point 2, Figs. 7.50 and 7.51.

ILLUSTRATION 7.15

Which of the following follow EAN rule.



a. **1st method: Neutral metal e^- count method.**

$$2\text{Mo} = 42 \times 2 = 84e^-$$

$$(\text{Mo} - \text{Mo}) \text{ bond} = 2e^-$$

$$(\text{Bridging halogens}) = \text{Each halogen } e^- \text{ donor} \\ = 3 \times 4 (\text{Cl}) = 12e^-$$

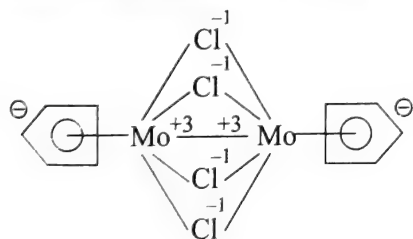
$$2(\text{Cyclopentadiene}) = 2 \times 5e^- = 10$$

$$\therefore \text{EAN} = 84 + 2 + 12 + 10 = \frac{108}{18} = 6$$

EAN should be 18 or multiple 18.

Hence it follows EAN rule.

2nd Method: Oxidation state e^- count method:



$$\text{Mo}^{+3} = (42 - 2) = 39$$

$$2\text{Mo}^{+3} = 39 \times 2 = 78e^-$$

$$(\text{Mo} - \text{Mo}) \text{ bond} = 2e^-$$

$$(\text{Bridging halide}) = \text{Each halogen } 4e^- \text{ donor} \\ = 4 \times 4 (\text{Cl}) = 16e^-$$

$$2(\text{Cyclopentadienyl anion}) = 2 \times 6e^- = 12e^-$$

$$\therefore \text{EAN} = 78 + 2 + 16 + 12 = \frac{108}{18} = 6$$

Hence it follows EAN rule.

b. **1st Method: Neutral metal e^- count method:**

$$2\text{Mo} = 42 \times 2 = 84e^-$$

$$(\text{Mo} \equiv \text{Mo}) = 2 \times 3 = 6e^-$$

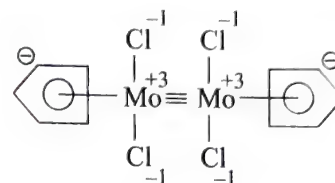
$$4(\text{Single bonded halogens}) = 1e^- \text{ donor} \\ = 4 \times 1 = 4e^-$$

$$2(\text{Cyclopentadiene}) = 2 \times 5e^- = 10e^-$$

$$\therefore \text{EAN} = 84 + 6 + 4 + 10 = 104 \text{ (Not multiple of 18)}$$

Hence does not follow EAN rule.

2nd Method: Oxidation state e^- count method:



$$2\text{Mo}^{+3} = 2(42 - 3) = 39 \times 2 = 78$$

$$(\text{Mo} \equiv \text{Mo}) \text{ bond} = 2 \times 3 = 6$$

$$4(\text{Single bonded halogen}) = \text{Each halogen } 2e^- \text{ donor} \\ = 2 \times 4 = 8e^-$$

$$2(\text{Cyclopentadienyl anion}) = 2 \times 4 = 8e^-$$

$$2(\text{Cyclopentadienyl anion}) = 2 \times 6 = 12e^-$$

$$\therefore \text{EAN} = 78 + 6 + 8 + 12 = 104 \text{ (Not multiple of 18)}$$

Hence does not follow EAN rule.

c. **1st Method: Neutral metal e^- count method:**

$$2\text{Mo} = 42 \times 2 = 84e^-$$

$$(\text{Mo} - \text{Mo}) \text{ bond} = 2e^-$$

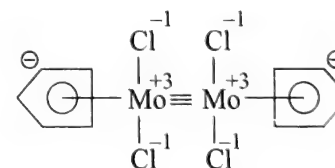
$$4(\text{Single bonded halogens}) = 1e^- \text{ donor} \\ = 4 \times 1 = 4e^-$$

$$2(\text{Cyclopentadiene}) = 2 \times 10 = 10e^-$$

$$\text{EAN} = 84 + 2 + 4 + 10 = 100 \text{ (Not multiple of 18)}$$

Hence does not follow EAN rule.

2nd Method: Oxidation state e^- count method:



$$2(\text{Mo}^{+3}) = (42 - 3) = 39 \times 2 = 78$$

$$(\text{Mo} - \text{Mo}) \text{ bond} = 2e^-$$

$$4(\text{Single bonded halogens}) = 2e^- \text{ donor} \\ = 4 \times 2 = 8e^-$$

$$2(\text{Cyclopentadienyl anion}) = 2 \times 6 = 12e^-$$

$$\therefore \text{EAN} = 78 + 2 + 8 + 12 = 100 \text{ (Not multiple of 18)}$$

Hence does not follow EAN rule.

d. **1st Method: Neutral metal e^- count method:**

$$2\text{Mo} = 42 \times 2 = 84e^-$$

$$(\text{Mo} - \text{Mo}) \text{ bond} = 2e^-$$

$$2(\text{Bridging halogens}) = \text{Each halogen } 3e^- \text{ donor} \\ = 3 \times 2 = 6e^-$$

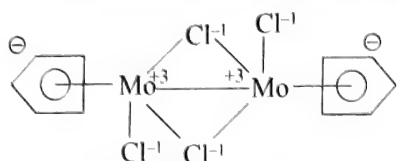
2(Single bonded halogens) = Each halogen $4e^-$ donor
 $= 1 \times 2 = 2e^-$

2(Cyclopentadiene) = $2 \times 5 = 10e^-$

\therefore EAN = $84 + 2 + 6 + 2 + 10 = 104$ (Not multiple of 18).

Hence does not follow EAN rule.

2nd Method: Oxidation state e^- count method:



$2(\text{Mo}^{+3}) = 2(42 - 3) = 39 \times 2 = 78e^-$ s

(Mo - Mo) bond = $2e^-$

2(Single bonded halogens) = Each halogen $2e^-$ donor
 $= 2 \times 2 = 4e^-$

2(Bridging halogens) = Each halogen $4e^-$ donor
 $= 2 \times 4 = 8e^-$

2(Cyclopentadienyl anion) = $2 \times 6 = 12e^-$

\therefore EAN = $78 + 2 + 4 + 8 + 12 = 104$ (Not multiple of 18).

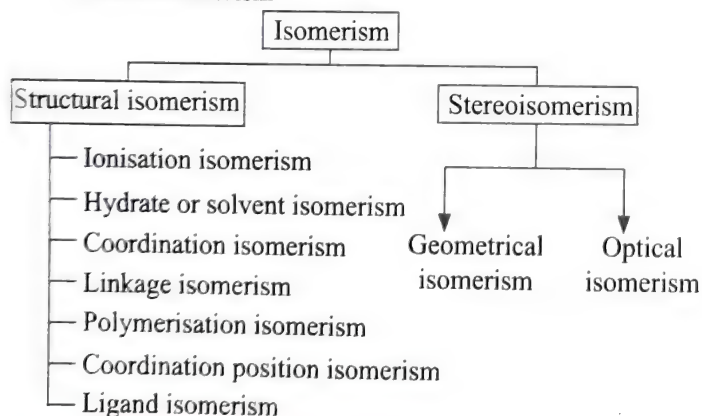
Hence does not follow EAN rule.

7.8 ISOMERISM IN COORDINATION COMPOUNDS

Complexes which have the same molecular or ionic formula, i.e. same chemical composition, but differ in structural arrangement of their atoms are called **isomers**. These isomers have different properties. The phenomenon that gives rise to different isomers is called isomerism.

Coordination compounds exhibit two main type of isomerism

- A. Structural isomerism
- B. Stereoisomerism



7.8.1 STRUCTURAL ISOMERISM

This isomerism arises in those complexes which have same molecular formula or chemical composition, but differ in structural or atom to atom bonding sequence.

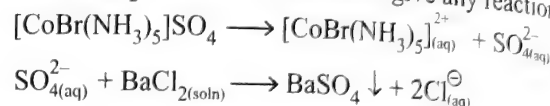
Structural isomerism is of the following types:

1. **Ionisation isomerism:** Complexes which have the same empirical formula but give different ions in solution or ionisation are called ionisation isomers and the phenomenon is called ionisation isomerism. It arises due to interchange of ligands in the coordination sphere and the ions present

outside the coordination sphere. This type of isomerism occurs when the counter ion in a coordination compound is itself a potential ligand, e.g.

- A. $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$
- B. $[\text{Co}(\text{NO}_3)(\text{NH}_3)_5]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{NO}_3$
- C. $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$ and $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$
- D. $[\text{CrI}_2(\text{NH}_3)_4]\text{Br}$ and $[\text{CrBrI}(\text{NH}_3)_4]\text{I}$

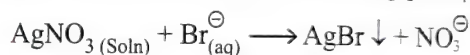
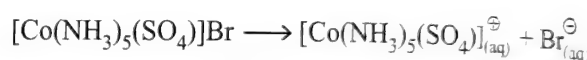
- a. **Qualitative analysis:** Ionisation isomers can be distinguished by qualitative analysis. In aqueous medium they ionise to form different ions in solution, e.g. $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$ (A) and $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$ (B). (A) gives a white precipitate of BaSO_4 when treated with BaCl_2 , whereas (B) does not give any reaction.



White ppt

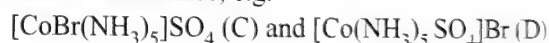
This indicates that SO_4^{2-} is present outside the coordination sphere.

- b. **With AgNO_3 solution:** (A) does not react with AgNO_3 solution but (B) gives pale yellow precipitate. This indicates that Br^- is present outside the coordination sphere in (II).

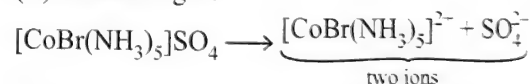


Pale yellow ppt.

- c. **Conductance method:** In aqueous medium, ionisation isomers ionise to give charged species. Greater is the number of ions (particles) or charges produced, greater is the conductance, e.g.

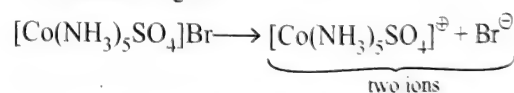


(C) ionises to give



i.e. two ions (or particles) and 4 charges (+2 and -2)

(D) ionises to give



i.e. two ions (or particles) and 2 charges (+1 and -1)

Since in (C) and (D), number of ions produced are same but (C) has more charges than (D). Thus (C) has more conductivity as compared to (D).

2. **Hydrate or solvent isomerism:** This type of isomerism is similar to ionisation isomerism. Water (H_2O) can be present in the complex in two ways:

- i. as a ligand, i.e. as a part of coordination entity.
- ii. as water of crystallisation, i.e. outside the coordination entity.

Hydrate isomers are obtained when H_2O molecule present as water of crystallisation are exchanged by the coordinated groups or ligand present in the coordination entity. Hydrate isomers have different physical and chemical properties.

For example, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ exists in three different isomeric forms:

Isomers	Colour
a. $[\text{CrCl}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$	
b. $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$	Green
c. $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Bluish green
d. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	Violet

Apart from their colours, the three isomers can be distinguished by **quantitative method** by reaction with AgNO_3 in aqueous medium.

- a. $[\text{CrCl}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O} \xrightarrow{\text{aq.}} [\text{CrCl}_3(\text{H}_2\text{O})_3]_{(\text{aq})}$
No precipitation of AgCl .
- b. $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O} \xrightarrow{\text{aq.}} [\text{CrCl}_2(\text{H}_2\text{O})_4]_{(\text{aq})}^{\oplus} + \text{Cl}_{(\text{aq})}^{\ominus}$
 $\text{Cl}_{(\text{aq})}^{\ominus} + \text{Ag}^{\oplus} \longrightarrow \text{AgCl} \downarrow$
- c. $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O} \longrightarrow [\text{CrCl}(\text{H}_2\text{O})_5]_{(\text{aq})}^{2+} + 2\text{Cl}_{(\text{aq})}^{\ominus}$
 $2\text{Cl}_{(\text{aq})}^{\ominus} + 2\text{Ag}^{\oplus} \longrightarrow 2\text{AgCl} \downarrow$
- d. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3 \longrightarrow [\text{Cr}(\text{H}_2\text{O})_6]_{(\text{aq})}^{3+} + 3\text{Cl}_{(\text{aq})}^{\ominus}$
 $3\text{Cl}_{(\text{aq})}^{\ominus} + 3\text{Ag}^{\oplus} \longrightarrow 3\text{AgCl} \downarrow$

With AgNO_3 , the three isomers (a), (b) and (c) give a white precipitate of AgCl in the molar ratio of 1: 2: 3 respectively, indicating the presence of 1, 2 and 3 moles of Cl^{\ominus} ions outside the coordination sphere.

These isomers can also be distinguished by **conductivity measurement method**, which will give different number of ionic species.

S. No.	Formulae	No. of ionic species	Charges
a.	$[\text{CrCl}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$	1	0
b.	$[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$	2	2(+1 and -1)
c.	$[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$	3	4(+2 and -2)
d.	$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	4	6(+3 and -3)

Since the number of ionic species produced is increasing in the order $a < b < c < d$, thus molar conductivity also increases in the same order i.e., $a < b < c < d$.

3. **Coordination isomers:** This isomerism is shown by those complexes which are composed of complex cation and complex anion. It arises due to interchange of ligands between the cationic and anionic complex entities. Some of the examples are as follows:

- a. $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ is isomeric with $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
- b. $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ is isomeric with $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$
- c. $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{SCN})_6]$ is isomeric with $[\text{Cr}(\text{NH}_3)_4(\text{SCN})_2][\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]$

In these pairs the central metal atom in the two coordination spheres may be same or different.

Distinction between coordination isomers:-

i. **Electrolysis methods:** Coordination isomers can be distinguished by electrolysis of an aqueous solution. In example (a) above, in first case cobalt complex migrates towards the negative electrode (anode) (\because Co complex is positively charged) and Co complex will be deposited at anode.

Cr will be deposited at positive electrode (cathode) since the Cr complex is negatively charged. Reverse will happen in its coordination isomer.

ii. **Conductivity method:** In example (c), the former isomer is (+3, -3) electrolyte and latter is (+1, -1) electrolyte, thus conductivity of the former isomer is greater than that of latter.

iii. These isomers can also be distinguished by X-ray diffraction and IR (infrared) spectroscopic method.

4. **Linkage isomerism:** This type of isomerism is shown by those coordination compounds which contain an ambidentate ligand, e.g., NO_2^{\ominus} , SCN^{\ominus} , CN^{\ominus} , $\text{S}_2\text{O}_3^{2-}$ etc. When an ambidentate ligand, having two different donor atoms coordinates to the central atom through either of its two donor atoms, two different complexes are obtained. and they are known as linkage isomers, the phenomenon is known as linkage isomerism.

For example, $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ and

$[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$. The two linkage isomers are different because they have different structures. $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ is yellow in colour, whereas $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ is red in colour.

The two linkage isomers are named as:

$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ pentaamminenitrito-N-cobalt(III)

chloride

$[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ pentaamminenitrito-O-cobalt(III)

chloride

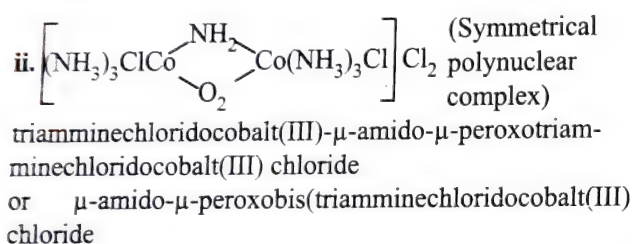
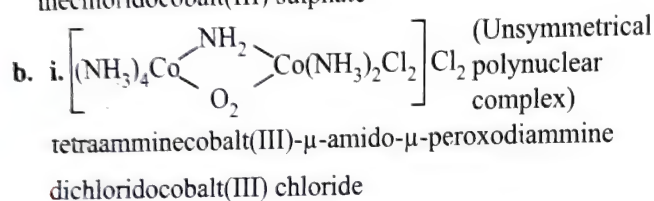
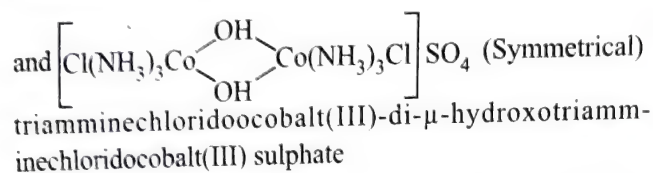
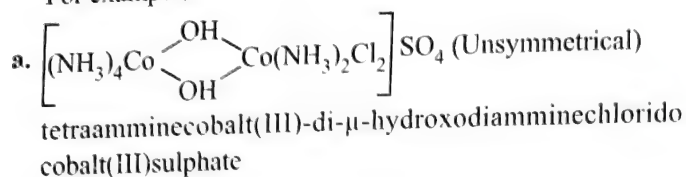
These isomers can be distinguished by UV, IR, NMR spectroscopic and X-ray diffraction methods.

5. **Polymerisation isomerism:** This type of isomerism exists among those complexes, which have the same empirical formula but each of the isomer is some simple multiple of the empirical formula, e.g.,

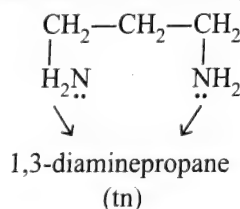
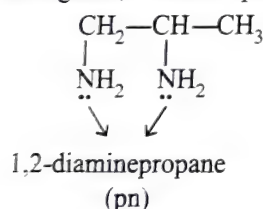
	$\text{Pt} : \text{NH}_3 : \text{Cl}$
a. i.	$[\text{PtCl}_2(\text{NH}_3)_2]$ 1 : 2 : 2
ii.	$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ 2 : 4 : 4 or 1: 2: 2
iii.	$[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2[\text{PtCl}_4]$ 3 : 6 : 6 or 1: 2: 2
	$\text{Co} : \text{NH}_3 : \text{NO}_2$
b. i.	$[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ 1 : 3 : 3
ii.	$[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ 2 : 6 : 6 or 1: 3: 3
	$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]_3[\text{Co}(\text{NO}_2)_6]_2$
	5 : 15 : 15 or 1: 3: 3

These isomers can be distinguished by mass spectroscopic methods.

6. Coordination position isomerism: This type of isomerism is shown in polynuclear complexes. This isomerism arises due to interchange of ligands between the coordination sphere of various central metal ion. Coordination position isomerism is thus a special type of coordination isomerism. For example,



7. Ligand isomerism: This type of isomerism arises because of the ligands, which are present in their isomeric forms, e.g.



Both are bidentate and neutral ligands. When these are coordinated to the metal atom, two isomers are obtained. These are called ligand isomers and the phenomenon is called ligand isomerism.

For example, $[\text{Co}(\text{pn})_2\text{Cl}_2]^{\oplus}$ and $[\text{Co}(\text{tn})_2\text{Cl}_2]^{\oplus}$

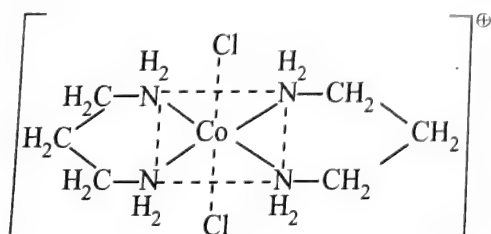
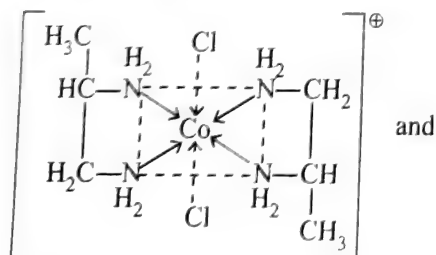


ILLUSTRATION 7.16

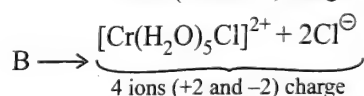
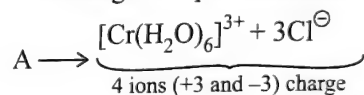
Describe a simple test to distinguish between the following pairs of compounds:

- (A) $[\text{Co}(\text{NH}_3)_5\text{Br}] \text{SO}_4$ and (B) $[\text{Co}(\text{NH}_3)_5\text{SO}_4] \text{Br}$
- (A) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and (B) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
- (A) *cis* $[\text{PtCl}_2(\text{NH}_3)_2]$ and (B) *trans* $[\text{PtCl}_2(\text{NH}_3)_2]$
- (A) and (B) Two enantiomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^{\oplus}$
- (A) $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{NO}_2)_6]$ and (B) $[\text{Cr}(\text{NH}_3)_4(\text{NO}_2)_2][\text{Cr}(\text{NH}_3)_2(\text{NO}_2)_4]$
- (A) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and (B) $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_2$
- (A) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and (B) $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$

Sol.

i. (A) and (B) are distinguished by qualitative method. (A) gives white precipitate of BaSO_4 with BaCl_2 solution due to the presence of SO_4^{2-} as counter ion. (B) gives pale yellow precipitate of AgBr (partially soluble in NH_4OH) with AgNO_3 solution due to the presence of Br^- ion as counter ion.

ii. (A) and (B) are distinguished by conductance method. (A) gives 4 ions with high charge whereas (B) gives 3 ions with low charge in aqueous solution as shown.



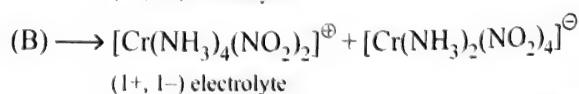
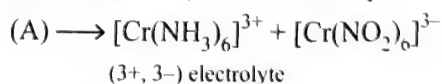
So, conductance of (A) will be higher than that of B.

Further (A) and (B) are also distinguished by **quantitative method**, with AgNO_3 (A) and (B) gives a white precipitate of AgCl in the molar ratio of 3: 2 respectively, indicating the presence of 3 and 2 moles of Cl^- as counter ions.

iii. (A) *cis* $[\text{PtCl}_2(\text{NH}_3)_2]$ has some value of dipole moment while the (B) *trans* $[\text{PtCl}_2(\text{NH}_3)_2]$ has zero value for its dipole moment.

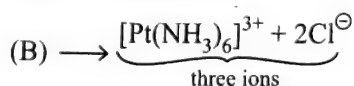
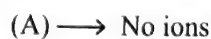
iv. One enantiomer of $[\text{Co}(\text{en})_2\text{Cl}_2]^{\oplus}$ is dextrorotatory (*d*-form) and the other enantiomer is levorotatory (*l*-form)

v. The given isomers can be distinguished by conductivity measurement, (A) conducts as (3+, 3-) electrolyte while (B) conducts as (1+, 1-) electrolyte.



Thus (A) has higher value of molar conductance than (B).

vi. (A) and (B) can be distinguished by conductance method. The ionisation of the given complex compounds can be shown as



Therefore (A) has zero value of its electrolytic conductance whereas (B) gives 3 ions, it has some value of electrolytic conductance.

- vii. (A) and (B) are distinguished by qualitative method. (A) gives white precipitate of BaSO_4 with BaCl_2 solution due to presence of SO_4^{2-} ion as counter ion. (B) gives white precipitate of AgCl (soluble in NH_4OH) with AgNO_3 solution due to the presence of Cl^- ion as counter ion.

ILLUSTRATION 7.17

Write hydrate isomers of the following and also give increasing order of the conductance of the isomers.

- a. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_3$ b. $[\text{Cu}(\text{H}_2\text{O})_4]\text{Cl}_2$

a. Hydrate isomers of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_3$ are:

- (A) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_3$
- (B) $[\text{Cr}(\text{H}_2\text{O})_5\text{Br}]\text{Br}_2 \cdot \text{H}_2\text{O}$
- (C) $[\text{Cr}(\text{H}_2\text{O})_4\text{Br}_2]\text{Br} \cdot 2\text{H}_2\text{O}$
- (D) $[\text{Cr}(\text{H}_2\text{O})_3\text{Br}_3] \cdot 3\text{H}_2\text{O}$

On ionisation the above hydrate isomers give

- (A) $\longrightarrow [\text{Cr}(\text{H}_2\text{O})_6]^{3+} + 3\text{Br}^-$ (4 ions)
- (B) $\longrightarrow [\text{Cr}(\text{H}_2\text{O})_5\text{Br}]^{2+} + 2\text{Br}^- + \text{H}_2\text{O}$ (3 ions)
- (C) $\longrightarrow [\text{Cr}(\text{H}_2\text{O})_4\text{Br}_2]^+ + \text{Br}^- + 2\text{H}_2\text{O}$ (2 ions)
- (D) No ions are formed.

Greater the number of ions formed, greater is the conductance. Hence, increasing order of conductance is $\text{D} < \text{C} < \text{B} < \text{A}$

b. Hydrate isomers of $[\text{Cu}(\text{H}_2\text{O})_4]\text{Cl}_2$ are

- (A) $[\text{Cu}(\text{H}_2\text{O})_3\text{Cl}]\text{Cl} \cdot \text{H}_2\text{O}$
- (B) $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$
- (C) $[\text{Cu}(\text{H}_2\text{O})_4]\text{Cl}_2$

On ionisation, the above hydrate isomers give

- (A) $\longrightarrow [\text{Cu}(\text{H}_2\text{O})_3\text{Cl}]^+ + \text{Cl}^-$ (2 ions)
- (B) \longrightarrow No ions
- (C) $\longrightarrow [\text{Cu}(\text{H}_2\text{O})_4]^{2+} + 2\text{Cl}^-$ (3 ions)

Greater the number of ions formed, greater is the conductance. Hence order of conductance is $\text{B} < \text{A} < \text{C}$.

7.8.2 GEOMETRICAL ISOMERISM

The complex compounds which have the same ligands in the coordination sphere but the relative position of the ligands round the central metal atom is different are called geometrical isomers and the phenomenon is called geometrical isomerism.

In a given complex compound the two ligands may occupy positions either adjacent to each other or opposite to each other. The complex compound having two ligands occupying the adjacent positions to each other is called *cis*-isomer while that in which the two ligands occupy opposite positions is called *trans*-isomer. Hence geometrical isomerism is also called *cis-trans* isomerism.

Geometrical isomers of a complex differ in physical characteristics such as dipole moment and visible/uv spectra.

7.8.2.1 Geometrical Isomerism in Complexes with C.N. 2 and 3

Geometrical isomerism is not found in complex compounds with coordination number 2 and 3, since in these cases all the positions occupied by the ligands round the central metal atom are adjacent to one another.

7.8.2.2 Geometrical Isomerism in Tetrahedral Complexes (C.N. = 4)

Geometrical isomerism cannot be shown by tetrahedral complexes, since all the four ligands in this geometry have adjacent position (i.e., *cis* position) to one another and all the four bond angles are the same ($= 109.5^\circ$).

7.8.2.3 Geometrical Isomerism in Square Planar Complexes (C.N. = 4)

Before discussing the geometrical isomerism exhibited by various types of square planar complexes, we should know how *cis* and *trans* isomers of a square planar complex are named. A square planar complex having similar ligands at adjacent positions (90° apart) is called *cis*-isomer while a square planar complex having two similar ligands at opposite positions (180° apart) is called *trans*-isomer. Thus a square planar complex having two similar ligands at 1-2, 2-3, 3-4 and 1-4 positions is called *cis*-isomer, while that having two similar ligands at 1-3 and 2-4 positions is called *trans*-isomer. *cis*- and *trans*-isomers are also named by numbering system. Thus in $[\text{Pd}^{2+}\text{Cl}_2\text{BrI}]^{2-}$ if two Cl^- ions are placed *cis* to each other or at 1-2 positions, it is named as *cis*-dichloro bromoiodo palladium (II) ion or 1,2-dichloro bromoiodo palladium (II) ion. On the other hand, if two Cl^- ions are placed *trans* to each other or at 1-3 positions, it is named as *trans*-dichlorobromoiodo palladium (II) ion or 1,3-dichlorobromoiodo palladium (II) ion (Fig. 7.1).

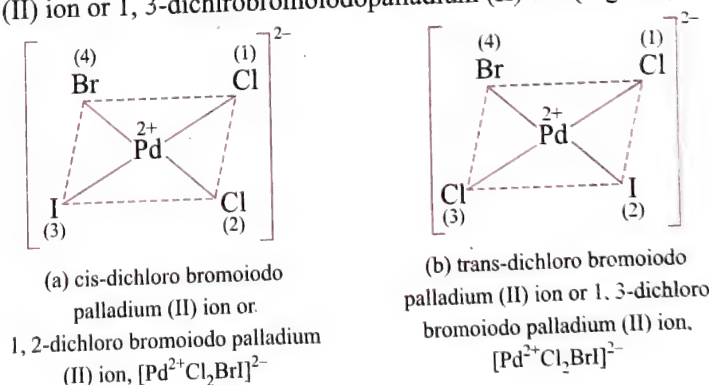


Fig. 7.1 Nomenclature of geometrical (*cis* and *trans*) isomers of a square planar complex.

Here we shall consider geometrical isomerism in square planar complexes of $[\text{Ma}_4]$, $[\text{Ma}_3\text{b}]$, $[\text{Mab}_3]$, $[\text{Ma}_2\text{b}_2]$, $[\text{Ma}_2\text{bc}]$, $[\text{Mabcd}]$ and $[\text{M}(\text{AB})_2]$ type in which M is the central metal atom; a, b, c and d are monodentate ligands and (AB) is an unsymmetrical bidentate ligand, since it has two different donor atoms namely A and B.

- Square planar complexes of $[\text{Ma}_4]$, $[\text{Ma}_2\text{b}_2]$ and $[\text{Mab}_3]$ type:** Square planar complexes of this type do not show geometrical isomerism, since all the possible spatial arrangement of four ligands round the central metal atom is the same.

2. Square planar complexes of $[Ma_2b_2]$ type. Important examples of square planar complexes of this type are $[Pt(NH_3)_2(Cl)_2]^0$, $[Pt(py)_2Cl_2]^0$, $[Pd(NH_3)_2(NO_2)_2]^0$ etc. These complexes exist in *cis*- and *trans*-isomers. These isomers of $[Pt^{2+}(NH_3)_2Br_2]^0$ are shown in Fig. 7.2. In (a) since both NH_3 molecules and both Br^- ions are *cis* to each other, it is called *cis*-isomer. On the other hand, in (b) since both NH_3 molecules and both Cl^- ions are *trans* with respect to each other, it is called *trans*-isomer.

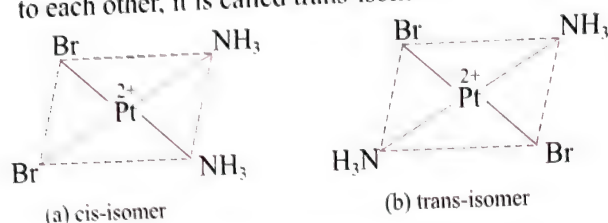


Fig. 7.2 *cis*- and *trans*-isomers of $[Pt^{2+}(NH_3)_2Br_2]^0$

3. Square planar complexes of $[Mabcd]$ type. Square planar complexes of this type exist in three isomeric forms. For example, $[Pt^{2+}(NH_3)(py)(Cl)(Br)]$ exists in three isomeric forms shown below in Fig. 7.3. These isomeric forms can be obtained by selecting one ligand, say NH_3 , and then placing the remaining three ligands, one by one *trans* to NH_3 .

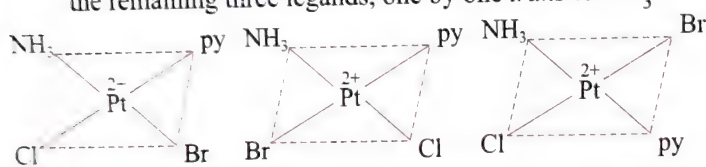


Fig. 7.3 Three isomeric forms of $[Pt^{2+}(NH_3)(py)(Cl)(Br)]$

$[Pt^{2+}(NO_2)(py)(NH_3)(NH_2OH)]^+$ and $[Pt^{2+}(C_2H_4)(NH_3)(Cl)Br]$ are other examples of square planar complexes which exist in three isomeric forms.

The existence of three isomeric forms in case of the complexes mentioned above indicates that these complexes have square planar geometry.

4. Square planar complexes of $[Ma_2bc]$ type. Square planar complexes of this type also show *cis-trans* isomerism. For example, $[Pd^{2+}Cl_2BrI]^{2-}$ ion exists in *cis*- and *trans*-isomers as shown below in figure.

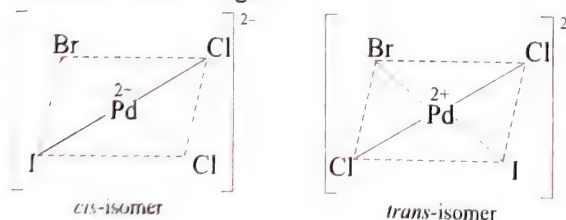


Fig. 7.4 *cis*- and *trans*-isomers of $[Pd^{2+}Cl_2BrI]^{2-}$ ion

$[Pt^{2+}(py)_2(NH_3)Cl]$ is another example of square planar complex of $[Ma_2bc]$ type which exists in *cis*- and *trans*-isomers.

5. Square planar complexes of $[M(AB)_2]$ type. Here M is the central metal ion and $[AB]$ represents an unsymmetrical bidentate ligand in which A and B are two different coordinating (donor) atoms. Square planar complexes of this type also exist in *cis*- and *trans*-isomers. For example, $[Pt^{2+}(gly)_2]$ exists in *cis*- and *trans*-isomers as shown in Fig. Here gly represents the glycinate ligand, $NH_2.CH_2COO^-$

which has N and O atoms as its donor atoms (i.e., A = N and B = O).

$[Cu^{2+}(gly)_2]^{10}$ is also an example of square planar complex of $[M(AB)_2]$ type. This complex also exhibits *cis-trans* isomerism.

7.8.2.4 Geometrical Isomerism in 6-coordinated Complexes: Octahedral Complexes

We know that a complex compound having central atom with coordination number equal to 6 is octahedral in shape. Before discussing the geometrical isomerism exhibited by various types of octahedral complexes, we should know how *cis*- and *trans*-isomers of an octahedral complex are named. In an octahedral complex, if two similar ligands are placed on any of the twelve edges of the octahedron, they are said to be in *cis* position. On the other hand, if two similar ligands are lying on a straight line which passes through the center (where the metal ion is placed),

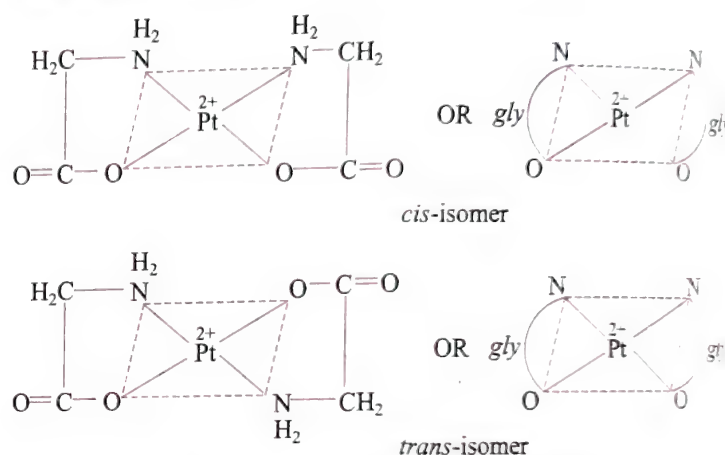


Fig. 7.5 *cis*- and *trans*-isomers of $[Pt^{2+}(gly)_2]$

they are said to be in *trans* position. Thus in an octahedral complex, the two ligands at positions 1-6, 2-4 and 3-5 are *trans* to each other and the two ligands occupying positions 1-2, 1-3, 6-4 etc. are *cis* to each other.

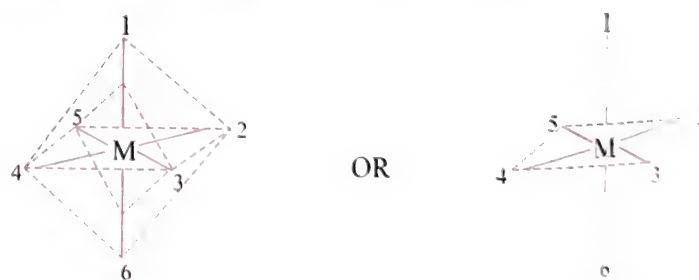


Fig. 7.6 Numbering of six ligands in a regular octahedral complex round the central metal ion, M.

The numbering system of ligands shown in Fig. 7.6 can be exemplified by considering the nomenclature of *cis*- and *trans*-isomers of $[Co^{3+}(NH_3)_4Cl_2]^+$ ion which is an octahedral complex ion. *Cis*-isomer of this ion in which two Cl^- ions are *cis* to each other is also called 1, 2-dichlorotetrammine cobalt (III) ion [See Fig. 7.7(a)]. Similarly, *trans*-isomer of this ion in which two Cl^- ions are *trans* to each other is also called 1, 6 dichlorotetrammine cobalt (III) ion. [See Fig. 7.7(b)]

Here we shall discuss the geometrical isomerism in octahedral complexes of the following type:

1. **Octahedral complexes of $[Ma_5]$ and $[Ma_5b]$ type:** Octahedral complexes of this type do not show geometrical isomerism.

2. **Octahedral complexes of $[Ma_4b_2]$ type:** Important examples of octahedral complexes of this type are $[Co^{3+}(NH_3)_4Cl_2]^+$, $[Co^{3+}(NH_3)_4(NO_2)_2]^+$ etc. These complexes exist in *cis*- and *trans*-isomers. These isomers of $[Co^{3+}(NH_3)_4Br_2]^+$ ion are shown in Fig. 7.7. In *cis*-isomer two Br^- ions occupy the adjacent (i.e., 1 and 2) positions of the octahedron while in *trans*-isomers these ions have the opposite (i.e., 1 and 6) positions. *Cis*-isomer of $[Co^{3+}(NH_3)_4Br_2]^+$ ion is yellow-brown while *trans*-form is yellow in colour.

(a) *cis*-isomer, (1, 2-dishlorotetrammine cobalt (III) ion), (yellow-brown)

(b) *Trans*-isomer (1, 6-dishlorotetrammines cobalt (III) ion), (yellow)

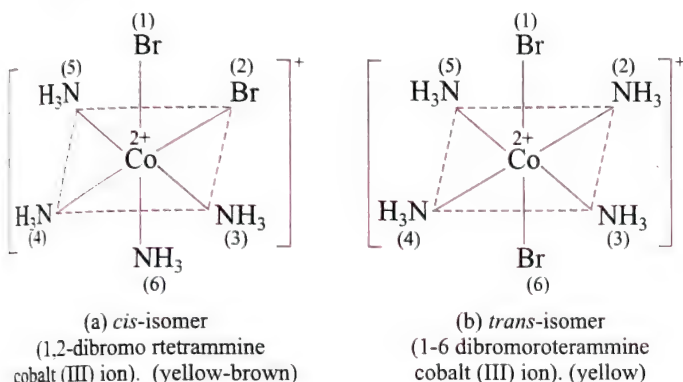


Fig. 7.7 *cis*- and *trans*-isomers of $[Co^{3+}(NH_3)_4Br_2]^+$ ion

3. **Octahedral complexes of $[Ma_3b_3]$ type:** We know that an octahedron has eight triangular faces and six corners (vertices). Octahedral complexes of $[Ma_3b_3]$ have two types of geometrical isomers:

(i) **Facial or fac isomer (*cis*-isomer):** In this isomer the three *a* groups occupy the three corners (vertices) of one triangular face while the other three *b* groups in this isomer take up the position of the remaining three vertices. This isomer is called facial or fac isomer. This isomer is also called *cis* isomer, since the three *a* groups are *cis* to each other. Similarly *b* groups are also *cis* to each other (See Fig. 7.8)

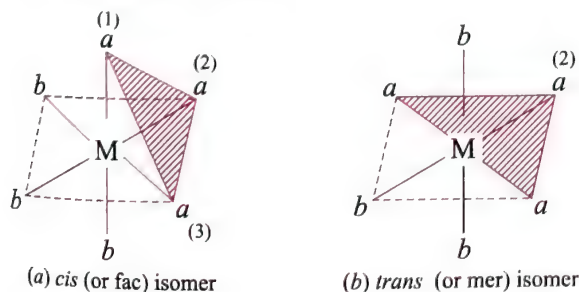


Fig. 7.8 *cis*- (or fac) and *trans* (or mer) isomers of Ma_3b_3 type octahedral complex

(ii) **Meridional or mer-isomer (*trans*-isomer):** In this isomer the three *a* groups are in one plane and the other three *b* groups are in a perpendicular plane, *a* and *b* groups lie along the meridian of a sphere (imagine our earth). Hence this isomer is called meridional or mer

isomer. In this isomer two of the three *a* groups and also two of the three *b* groups are *trans* to each other (See Fig. 7.8). Hence this isomer is also called *trans* isomer.

Examples: $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_3(NO_2)_3]$, $[Cr(H_2O)_3F_3]$, $[Cr(MH_3)_3Cl_3]$, $[Rh(py)_3Cl_3]$, $[Ru(H_2O)_3Cl_3]$, $[Ir(H_2O)_3Cl_3]$, $[Pt(NH_3)_3Br_3]^+$, $[Pt(NH_3)_3I_3]^+$ etc. are important examples of octahedral complexes of Ma_3b_3 type. *Cis*-(fac) and *trans*-(mer) isomers of $[Co(NH_3)_3Br_3]$ are given in Fig. 7.9.

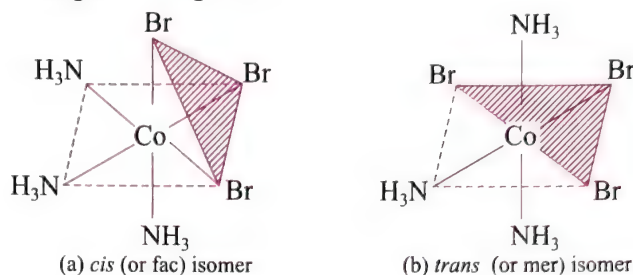


Fig. 7.9 *cis* (fac) and *trans* (mer) isomers of $[Co(NH_3)_3Br_3]$ octahedral complex

$[Co(NH_2CH_2COO)_3]$ also has two geometrical isomers, viz., facial and meridional (See Fig. 7.10). In the given complex N and O atoms are the donor atoms.

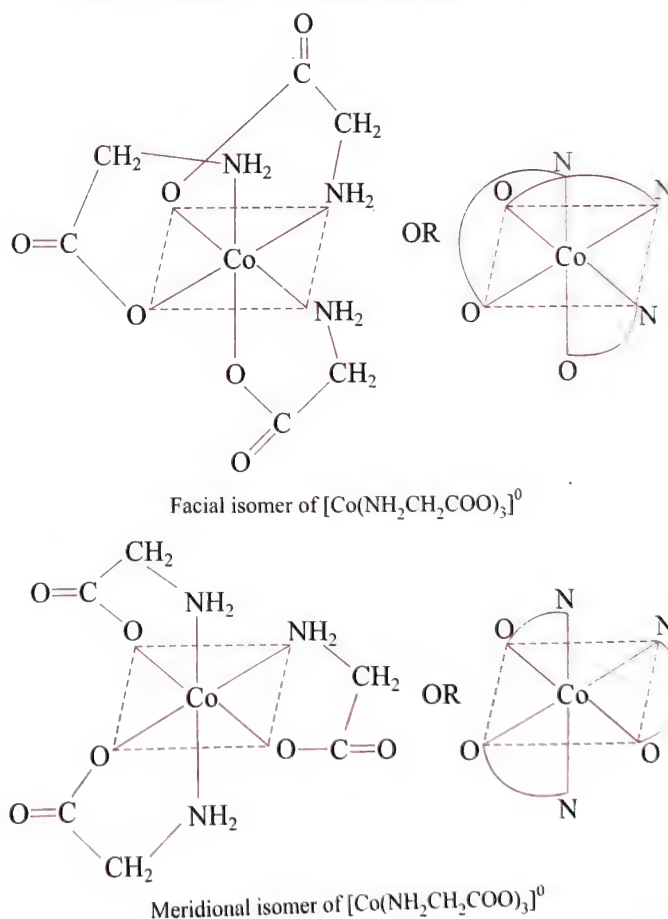


Fig. 7.10 Facial and meridional isomers of $[Co(NH_2CH_2COO)_3]^0$

4. **Octahedral complexes of $[Ma_4bc]$ type:** $[Co^{3+}(NH_3)_4(H_2O)Br]^{2+}$ ion is an important example of octahedral complex of $[Ma_4bc]$ type. This ion has *cis*- and *trans*-isomers whose structures are given in Fig. 7.11. In *cis*-form two NH_3 molecules have *cis* positions to each other and in *trans*-form these ligands (i.e., two NH_3 molecules) have *trans* positions with each other.

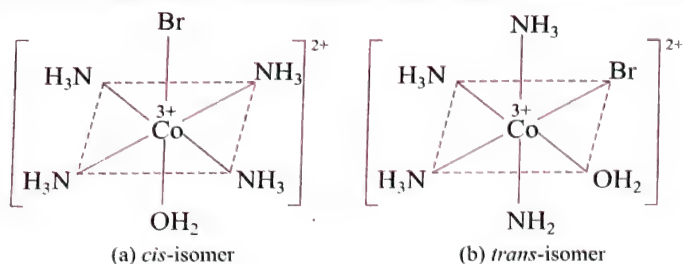


Fig. 7.11 Structure of *cis-* and *trans-*isomers of $[\text{Co}^{3+}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]^{2+}$ octahedral complex ion.

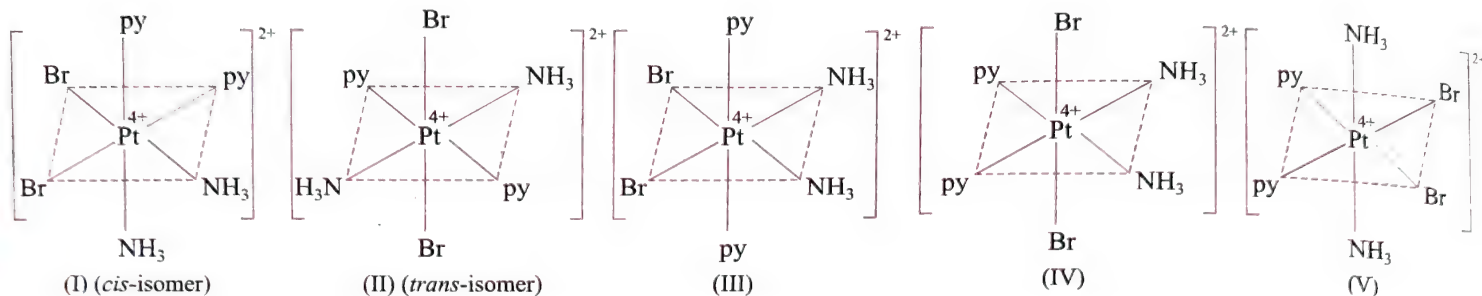


Fig. 7.12 All possible five geometrical isomers of $[\text{Pt}^{4+}(\text{NH}_3)_2(\text{py})_2\text{Br}_2]^{2+}$ ion

- 6. Octahedral complexes of $[\text{Mabcdef}]$ type:** Octahedral complexes which have different monodentate ligands have been prepared for Pt (IV), $[\text{Pt}^{4+}(\text{py})(\text{NH}_3)(\text{NO}_2)(\text{Cl})(\text{Br})(\text{I})]$ is the only complex of this type of complexes. Theoretically 15 geometrical isomers are possible for this complex compound. In fact only three geometrical isomers have been isolated.
- 7. Octahedral complexes of $\text{M}(\text{AA})_3$ type:** Octahedral complexes of this type of do not show geometrical isomers.
- 8. Octahedral complexes of $[\text{M}(\text{AA})_2\text{a}_2]$ type:** Here (AA) represents a symmetrical bidentate ligand in which A and A are two identical coordinating (donor) atoms, $[\text{Co}(\text{en})_2\text{Cl}_2]^{+}$, $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$, $[\text{Co}(\text{en})_2(\text{NO}_3)_2]^{+}$, $[\text{Cr}(\text{en})_2\text{Cl}_2]^{+}$, $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{-}$, $[\text{Ir}^{4+}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{2-}$ etc. are the examples of octahedral complex ions of $[\text{M}(\text{AA})_2\text{a}_2]$ type. Each of these complex ions exists in *cis-* and *trans-*isomers. As an example *cis-* and *trans-*isomers of $[\text{Co}^{3+}(\text{en})_2\text{Br}_2]^{+}$ ion are shown in Fig. 7.13.

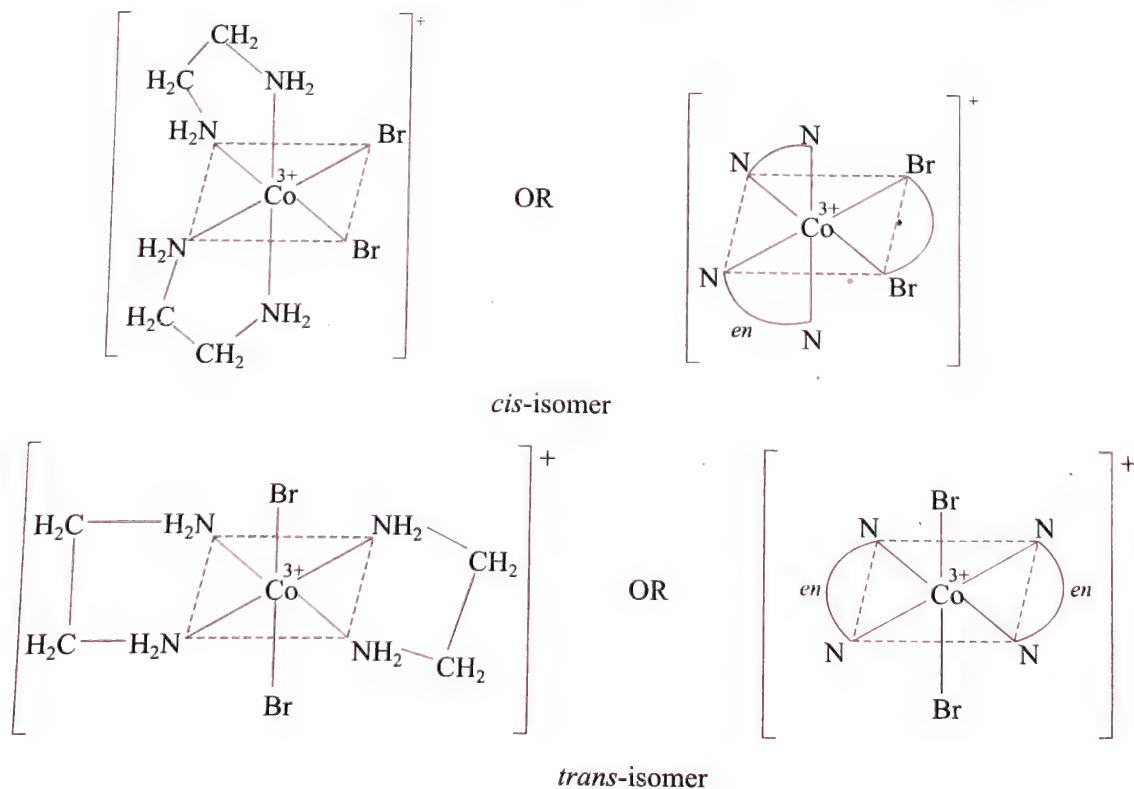
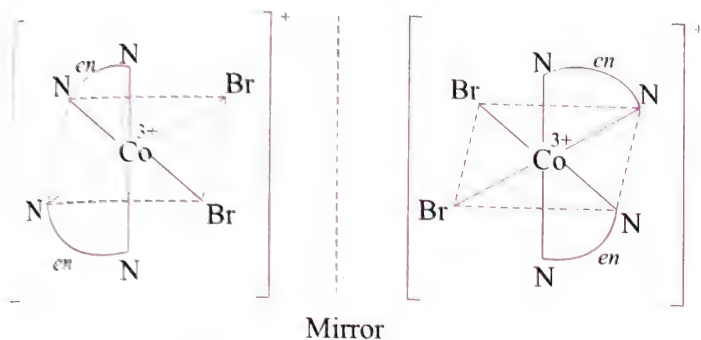
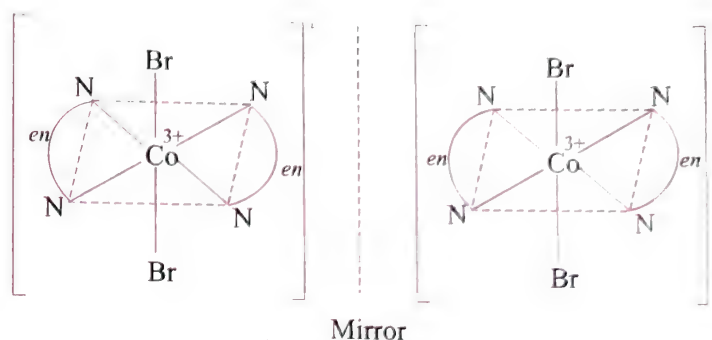


Fig. 7.13 *cis-* and *trans-*isomers of $[\text{Co}^{3+}(\text{en})_2\text{Br}_2]^{+}$ ion

Symmetrical/unsymmetrical nature of *cis*- and *trans*-isomers: The structures of mirror images of *cis*- and *trans*-forms of $[\text{Co}^{3+}(\text{en})_2\text{Br}_2]^+$ ion are given at (a) and (b) of Fig. 7.14 respectively. Since the structure of *cis*-isomer and its mirror image are non-super imposable on each other, *cis*-isomer is unsymmetrical. On the other hand, since the structure of *trans*-form and its mirror image are super-imposable on each other, *trans*-isomer is symmetrical. Thus *cis*-isomer is optically active but *trans*-isomer is optically inactive.



(a) Structure of *cis*-isomer of $[\text{Co}(\text{en})_2\text{Br}_2]^+$ and its mirror image



(b) Structure of *trans*-isomer of $[\text{Co}(\text{en})_2\text{Br}_2]^+$ ion and its mirror image

Fig. 7.14 Structure of *cis*- and *trans*-forms of $[\text{Co}(\text{en})_2\text{Br}_2]^+$ ion and their mirror images.

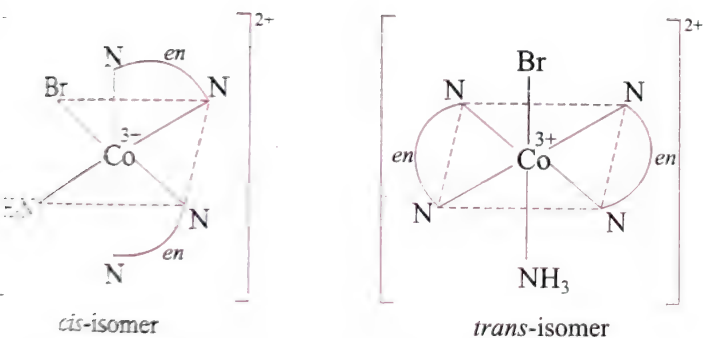


Fig. 7.15 *cis*- and *trans*-isomers of $[\text{Co}^{3+}(\text{en})_2(\text{NH}_3)(\text{Br})]^{2+}$ ion

As in case of $[\text{Co}^{3+}(\text{en})_2\text{Cl}_2]^+$ ion, the *cis*-isomer of $[\text{Co}^{3+}(\text{en})_2(\text{NH}_3)(\text{Cl})]^{2+}$ is also unsymmetrical while its *trans*-isomer is symmetrical. Thus *cis*-form is optically active while *trans*-isomer is optically inactive.

10. **Octahedral complexes of $[\text{M}(\text{AA})_2\text{b}_2]$ type:** In this complex AA represents a bidentate ligand in which two A atoms are donor atoms, *a* and *b* are monodentate ligands. Octahedral complexes of $[\text{M}(\text{AA})_2\text{b}_2]$ type exist in three geometrical isomers.

(i) **One *cis*-isomer:** In this isomer the two *a* groups are *cis* to each other. Similarly, the two *b* groups are also *cis* to each other. This isomer is unsymmetrical and has no mirror plane passing through the metal (M) or centre of inversion. Being unsymmetrical, this isomer is optically active.

(ii) **Two *trans*-isomers:** In one *trans*-isomer the two *a* groups are *trans* to each other and the two *b* groups are *cis* to each other. In the other *trans*-isomer the two

9. Octahedral complexes of $[\text{M}(\text{AA})_2\text{ab}]$ type:

$[\text{Co}^{3+}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ is an important example of octahedral complex of $[\text{M}(\text{AA})_2\text{ab}]$ type. This complex ion exists in *cis*- and *trans*-isomers. In *cis*-isomer the two monodentate ligands viz., NH_3 and Cl^- occupy the adjacent (i.e., *cis*) positions while in *trans*-isomer these ligands occupy opposite (i.e., *trans*) position (See Fig. 7.15). $[\text{Ru}^{3+}(\text{C}_3\text{O}_4)_2(\text{py})(\text{NO}_2)]^{2-}$ also exists in *cis*- and *trans*-isomers.

a groups are *cis* to each other and the two *b* groups are *trans* to each other. Both these isomers have mirror plane passing through the metal (M). AA and *a*, *a/b*, *b* and hence these give only super imposable mirror image. Both these isomers are symmetrical and hence are optically inactive, i.e., achiral.

Examples: $[\text{Co}^{3+}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ and $[\text{Co}^{3+}(\text{C}_2\text{O}_4)(\text{NH}_3)_2(\text{NO}_2)_2]^-$ are important examples of octahedral complex of $[\text{M}(\text{AA})_2\text{b}_2]$.

Geometrical isomers of $[\text{Co}^{3+}(\text{en})(\text{NH}_3)_2\text{Br}_2]^+$ ion. This ion is an octahedral ion of $[\text{M}(\text{AA})_2\text{b}_2]$ type. This ion has three geometrical isomers.

(i) **One *cis*-isomer.** In this isomer two NH_3 ligands are *cis* to each other. Similarly, the two Br^- ligands are also *cis* to each other. [See Fig. 7.16]. This isomer is unsymmetrical and has no mirror plane passing through the metal or centre of inversion. Being unsymmetrical this isomer is optically active.

(ii) **Two *trans*-isomers.** In one *trans*-isomer two NH_3 ligands are *trans* to each other and two Br^- ligands are *cis* to each other (See Fig. 7.16). In the other *trans*-isomer two NH_3 ligands are *cis* to each other and two Br^- ligands are *trans* to each other (See Fig. 7.16). Both these isomers have mirror plane passing through the metal, en and NH_3 , NH_3/Br^- , Br^- and hence these give only super-imposable mirror image. Both these isomers are symmetrical and are, therefore, optically inactive, i.e., achiral.

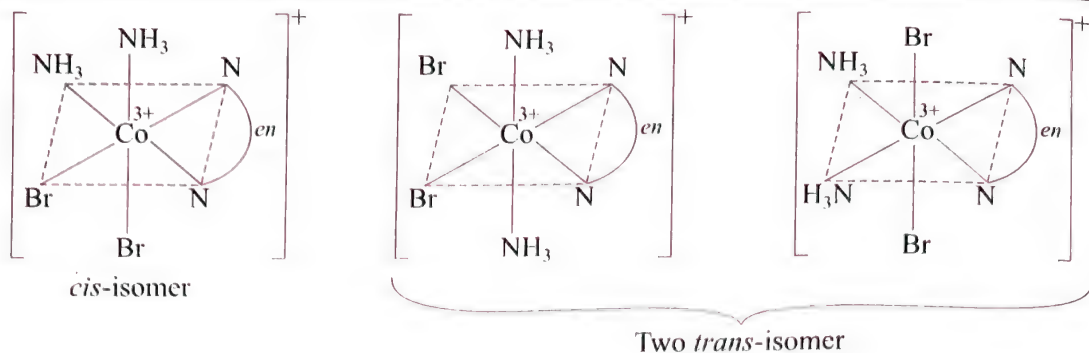


Fig. 7.16 cis- and trans-isomers of $[\text{Co}^{3+}(\text{en})(\text{NH}_2)_2\text{Br}_2]^+$ ion

11. Octahedral complexes of $[\text{M}(\text{AB})_3]$ type: Here (AB) represents an unsymmetrical bidentate ligand in which A and B are two different coordinating (donor) atoms. Octahedral complexes of this type exist in *cis*- and *trans*-isomers. As an example, the *cis*- and *trans*-isomers of $[\text{Cr}^{3+}(\text{gly})_3]$ have been shown in Fig. 7.17. Each of these forms is optically active and hence each has a pair of optical isomers. In *cis*-isomers two N-atoms and two O-atoms of two gly ions are placed at *cis*-positions while in *trans*-isomer these atoms are occupying *trans*-positions.

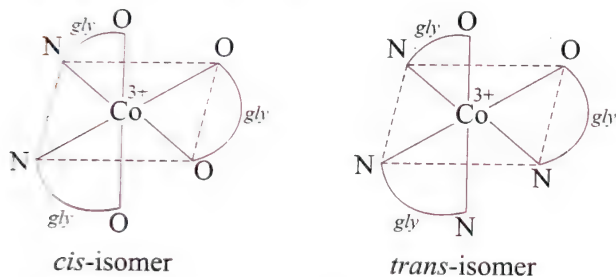


Fig. 7.17 cis- and trans-isomers of $[\text{Cr}^{2+}(\text{gly})_3]$

Since both the forms (i.e., *cis*- and *trans*-forms) are optically active, each of these forms had *d*- and *l*-forms (optical isomers).

7.8.2.5 Optical (or *d-l* or Mirror-Image) Isomerism

Before discussing the optical isomerism shown by various type of complexes we will define some important terms related to this isomerism.

1. Optical activity and optically active complexes: When the solutions of certain complex compounds are placed in the path of a plane-polarized light (the waves of the plane-polarized light vibrate only in one direction; vibrations in other directions are cut off), they rotate its plane through a certain angle which may be either to the left or to the right. This property of a complex of rotating the plane of polarized light is called its optical activity and the complex possessing this property is said to be optically active.

2. Different forms of optically active complexes: Optically active complexes are said to exist in the following forms:

- (i) The isomer which rotates the plane of polarized light towards right (i.e., in clockwise direction) is said to be dextrorotatory or *d*-form, *d*-form is also represented by placing (+) sign before its name or formula.

- (ii) The isomer which rotates the plane of polarized light towards left (i.e., in anti-clockwise direction) is called levorotatory or *l*-form, *l*-form is also represented by putting (−) sign before its name or formula, (+), dextro, and (−), levo, refer to the sign of rotation of the optical isomer at the sodium D line wavelength. The *d*- and *l*-forms have the following characteristics:

- (a) Since *d*- and *l*-forms are capable of rotating the plane of polarized light, these are said to be optically active forms or optical isomers and this phenomenon is called optical activity or optical isomerism. These two forms have exactly identical physical and chemical properties, although they differ in their action on polarized light.
- (b) *d*- and *l*-forms are mirror images to each other just as left hand is the mirror image of the right hand. Thus *d*- and *l*-forms can be superimposed on each other and hence *d*- and *l*-forms are also called mirror-image isomers. These optical isomers are also called optical antipodes or enantiomorphs (Latin: enantio = opposite; morphs = forms) or enantiomers. From this description it follows that optical isomerism can also be called mirror-image isomerism or enantiomorphism or enantiomerism.

- (iii) The isomer which is not capable of rotating the plane of polarized light is called optically inactive. Such an isomer is called meso, racemic, *dl*- or (±) form. A racemic substance is composed of 50% *d*- and 50% *l*-form. The solution of a racemic (*dl* mixture) form in a solvent which contains equimolecular amounts of *d*- and *l*-forms is symmetrical and hence optically inactive, because the rotation (of the plane of polarized light) produced by one isomer, *d*-isomer, is balanced or compensated by equal but opposite rotation produced by the other (i.e., *l*-isomer). Optical inactivity produced in *dl*-mixture said to be due to external compensation.

3. Condition for a molecule to show optical isomerism: A molecule in which the grouping of the atoms is asymmetric is called an *asymmetric* or *dissymmetric molecule*. An asymmetric molecule has the following features:

- (i) An asymmetric molecule never has a plane of symmetry (also called mirror-image plane) which is defined as an imaginary plane dividing the molecule in such a way that

the part of it on one side of the plane is the mirror image of that on the other side of the plane. The molecules possessing such a plane of symmetry are always inactive while those having no plane of symmetry are optically active and hence show optical isomerism.

- (ii) An asymmetric molecule cannot be superimposed on its mirror image.

Thus the most necessary and sufficient condition for a molecule to show optical isomerism (i.e., to exist in *d*- and *l*-forms) is that the molecule should be asymmetric, (i.e., it should have no plane of symmetry) and should be not be superimposable on its mirror image.

7.8.2.6 Optical Isomerism in Tetrahedral Complex (C.N. = 4)

Here we shall discuss optical isomerism in the following of tetrahedral complexes.

- 1. Tetrahedral complexes of $[Ma_4]$, $[Ma_2b_2]$ and $[Ma_3b]$ type:** Tetrahedral complexes of $[Ma_4]$, $[Ma_2b_2]$ and $[Ma_3b]$ type are not able to show optical isomerism because all the possible arrangements of the ligands round the central metal ion, M, are exactly equivalent.

- 2. Tetrahedral complexes of $[Mabcd]$ type:** Since the central atom (M) in tetrahedral complexes of $[Mabcd]$ type is surrounded by four different ligands, the tetrahedral complex of this type is expected to produce a pair of enantiomorphs. For example, $[As^{3+}(CH_3)(C_2H_5)(S)(C_6H_4COO)]^{2-}$ ion (tetrahedral) exists in two optical isomers as shown in Fig. 7.18.

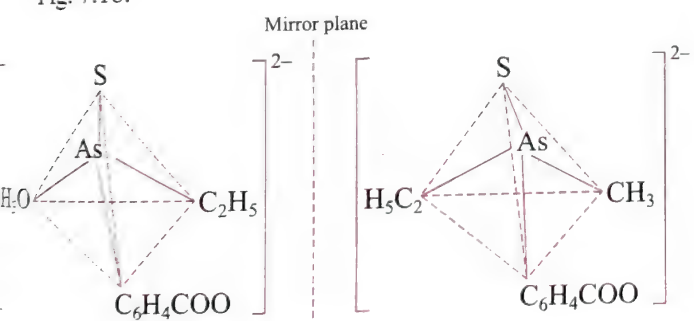


Fig. 7.18 Optical isomers of tetrahedral complex ion, $[As(CH_3)(C_2H_5)(S)(C_6H_4COO)]^{2-}$

Here it may be noted that 4 different groups the central metal ion are not the only requirement to make the complex to show mirror-image isomerism. All that is required is that the molecule should be asymmetric (i.e., unsymmetrical), i.e., it should have no plane of symmetry so that it can exist in two mirror-image forms.

- 3. Tetrahedral complexes of Be (II), B (III) and Zn (II)** with symmetrical bi-dentate ligands have been made and resolved into optical isomers. Some examples of tetrahedral complexes of this type are *bis* (salicylaldehydato) boron (III) ion, $[B^{3+}(C_6H_4 \cdot O \cdot CHO)_2]^+$ and *bis* (benzoylacetonato) beryllium (II), $[Be^{2+}(C_6H_5CO \cdot CH \cdot CH_3CO)_2]^0$ whose mirror-image isomer are given in Fig. 7.19 and 7.20 respectively.

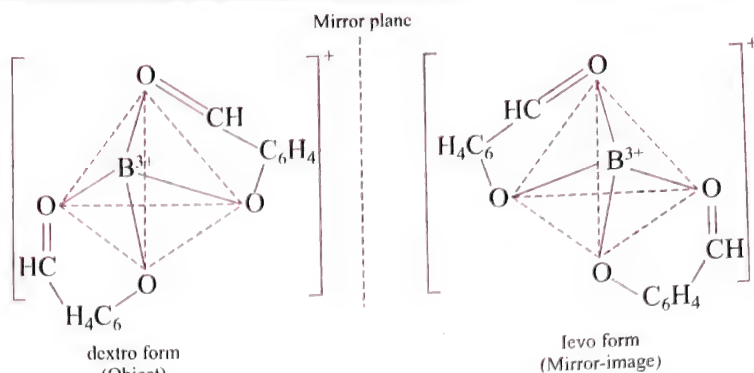


Fig. 7.19 Mirror-image isomers of tetrahedral bis (salicylaldehydato) boron (III) ion, $[B^{3+}(C_6H_4 \cdot O \cdot CHO)_2]^+$

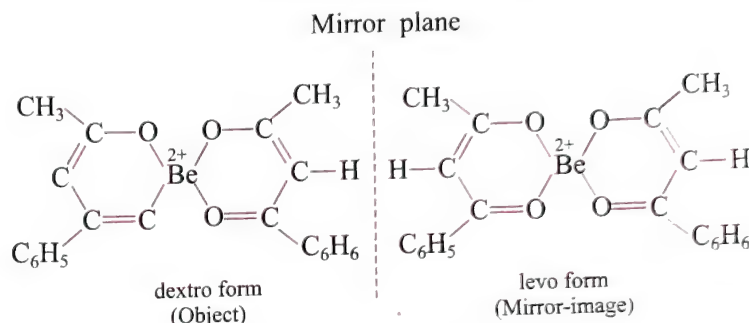


Fig. 7.20 Mirror-image isomers of tetrahedral bis (benzoylacetonato) beryllium (II) ion, $[Be^{2+}(C_6H_5CO \cdot CH \cdot CH_3CO)_2]^0$

7.8.2.7 Optical Isomerism in Square Planar Complexes (C.N. = 4)

Optical isomerism rarely occurs in square planar complexes, since they have all the four ligands and the central metal ion in the same plane and hence contain a plane or axis of symmetry. Thus these complexes are optically inactive, i.e., they cannot show optical isomerism even if all the four ligands are different.

7.8.2.8 Optical Isomerism in Six-Coordinated Complexes

Octahedral complexes: Here we shall discuss the optical in octahedral complexes of the following type:

- 1. Octahedral complexes of $[Ma_6]$ and $[Ma_5b]$ type:** Complexes of this type do not show optical isomerism.
- 2. Octahedral complexes of $[Ma_4b_2]$ and $[Ma_3b_3]$ type:** (a) We have already seen that octahedral complexes of $[Ma_4b_2]$ type exist in *cis*- and *trans*-isomers. Both these isomers are optically inactive due to the presence of symmetry and hence do not show optical isomerism, (b) We have already mentioned that octahedral complexes of $[Ma_3b_3]$ type exist in *cis* (or facial) and *trans* (or meridional) isomers. Both these isomers are optically inactive and hence do not show optical isomerism.
- 3. Octahedral complexes of $[Ma_2b_2c_2]$ type:** Complexes of this type do not show optical isomerism.
- 4. Octahedral complexes of $[Ma_2b_2c_2]$ type:** $[Pt^{4+}(NH_3)_2(py)_2Br_2]^{2+}$ ion is an important example of octahedral complex of $[Ma_2b_2c_2]$ type. We have already stated that $[Pt^{4+}(NH_3)_2(py)_2Br_2]^{2+}$ ion can exist theoretically in five geometrical isomers, but only three have been

isolated. In *cis*-isomer two identical ligands occupy the adjacent positions of the octahedron. This *cis*-isomer exists in two optical (mirror-image) isomers which are mirror-image to each other as shown in Fig. 7.21. *Trans*-form of this complex ion is symmetrical and hence is optically inactive form. Thus it is *trans-meso* form.

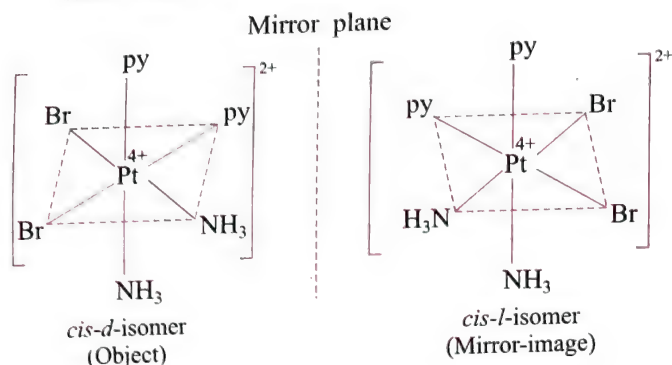


Fig. 7.21 Mirror-image isomers of $[\text{Pt}^{4+}(\text{NH}_3)_2(\text{py})_2\text{Br}_2]^{2+}$ ion

5. **[Mabcdef] type complexes:** $[\text{Pt}^{4+}(\text{py})(\text{NH}_3)(\text{NO}_2)\text{ClBr}_2]^{0}$ is the only example of octahedral complex of this type. We have already stated that, theoretically, this complex can exist in 15 geometrical isomers. Each of these 15 geometrical isomers exists in optically active *d*- and *l*-forms, giving a total of 30 optically active isomers, *d*- and *l*-isomers for one of the 15 geometrical isomers are given in Fig. 7.22.

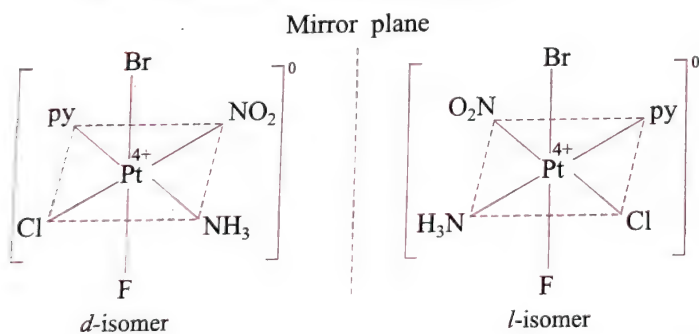


Fig. 7.22 Optical (*d*- and *l*-) forms of $[\text{Pt}^{4+}(\text{py})(\text{NH}_3)(\text{NO}_2)(\text{Cl})(\text{Br})(\text{I})]^{0}$

6. **[M(AA)₃] type complexes:** Due to the absence of a plane

or centre of symmetry, the octahedral complexes of this type are resolvable into dextro and levo forms. For example, *d*- and *l*-forms of $[\text{Co}^{3+}(\text{en})_3]^{3+}$ ion are shown in Fig. 7.23. Other examples of octahedral complexes of $[\text{M}(\text{AB})_3]$ type which exist in *d* and *l* forms are: $[\text{Cr}^{3+}(\text{ox})_3]^{3-}$, $[\text{Co}^{3+}(\text{pn})_3]^{3+}$, $[\text{Pt}^{4+}(\text{en})_3]^{4+}$, $[\text{Fe}^{2+}(\text{diph})_3]^{2+}$ etc. The fact that the complexes of $[\text{M}(\text{AA})_3]$ type can be resolved into optical isomers confirms that these complexes have octahedral shape. Neither hexagonal nor trigonal prismatic geometry of 6-coordinated complex can give rise to activity.

7. **[M(AA)₂A₂] type complexes:** Here we can consider $[\text{Co}^{3+}(\text{en})_2\text{Cl}_2]^{+}$ ion. We have already stated that this ion shows geometrical isomerism and hence exists as *cis*- and *trans*-isomers. The *cis*-isomer does not have any plane or centre of symmetry and hence is optically active, i.e., *cis*-isomer can be resolved into two optically active isomers (*d*- and *l*-isomers). On the other hand, the *trans*-isomer has a plane of symmetry and hence is optically inactive, i.e., it cannot be resolved into optically active isomers.

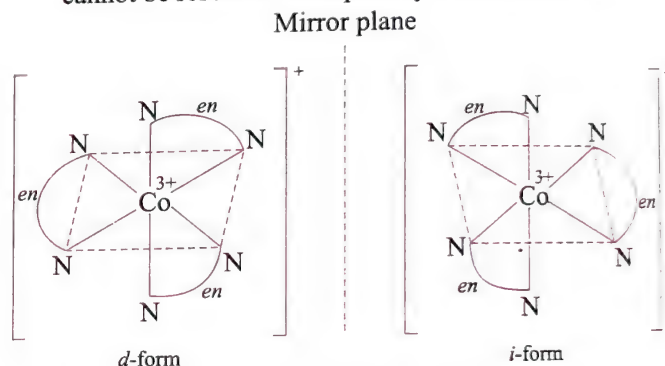


Fig. 7.23 Optical isomers of $[\text{Co}^{3+}(\text{en})_2\text{Cl}_2]^{+}$ ion. These cannot be superimposed on each other

Thus *trans*-isomer is optically inactive (*meso*-form). Consequently $[\text{Co}(\text{en})_2\text{Br}_2]^{+}$ ion has three optical isomers viz. (a) Two optically active isomers corresponding to *cis*-configuration (i.e., *d*- and *l*-forms). One form is the mirror image of the other. (b) One optically inactive form corresponding to *trans*-form (*meso*-form). All the three forms have been shown in Fig. 7.24.

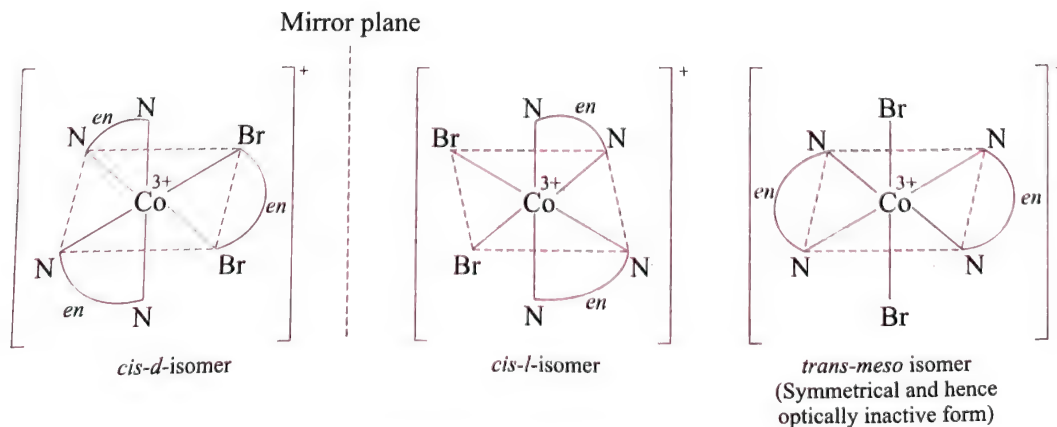
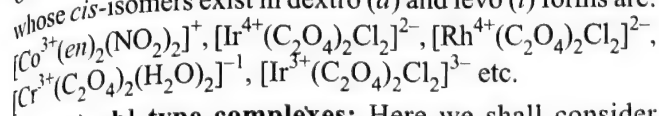


Fig. 7.24 Optical isomers of $[\text{Co}(\text{en})_2\text{Br}_2]^{+}$ ion

Other examples of $[M(AA)_2a_2]$ type octahedral complexes whose *cis*-isomers exist in dextro (*d*) and levo (*l*) forms are:



8. **$[M(AA)_2ab]$ type complexes:** Here we shall consider $[Co^{3+}(en)_2(NH_3)Br]^{2+}$ ion. We have already seen that this ion

exists in *cis*- and *trans*-isomers (geometrical isomers). Due to the absence of plane or centre of symmetry in *cis*-isomer, this isomer is optically active and hence can be resolved into *d*- and *l*-forms. On the other hand, the *trans*-isomer has a plane of symmetry and hence is optically inactive, i.e., *trans*-isomer is *meso-trans* isomer (See Fig. 7.25).

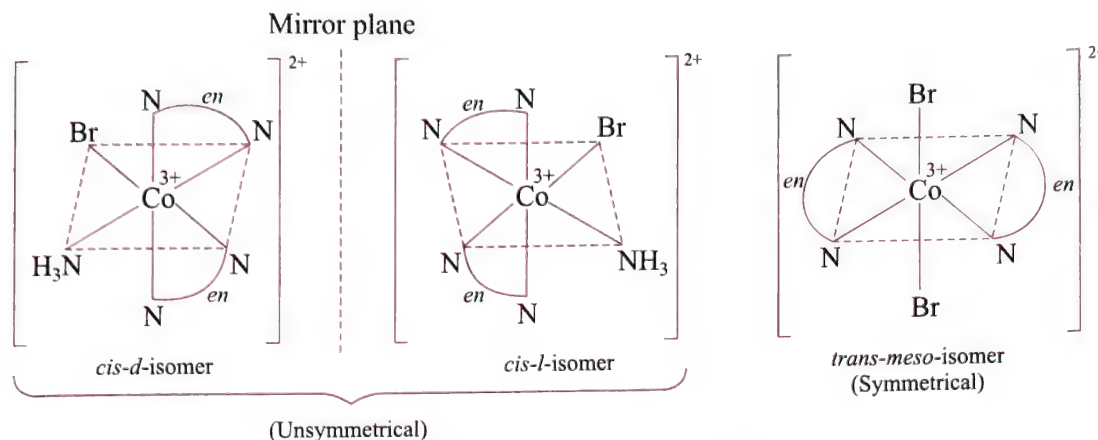


Fig. 7.25 Optical isomers of $[Co^{2+}(en)_2(NH_3)Br]^{2+}$ ion

Another example of $[M(AA)_2ab]$ type octahedral complexes whose *cis*-isomer exists in *d*- and *l*-forms is $[Rh^{3+}(C_2O_4)_2(py)(NO_2)]^{2-}$.

9. **$[M(AA)a_2b_2]$ type complexes:** Here we shall consider $[Co^{3+}(en)(NH_3)_2Br_2]^{\oplus}$ ion. We have seen that this ion exists in *cis*- and *trans*-isomers (geometrical isomers). *Cis*-isomer is optically active and hence gives optically active *d*- and *l*-forms. On the other hand *trans*-isomer is optically inactive and hence does not give any optical active isomer, (See Fig. 7.26).

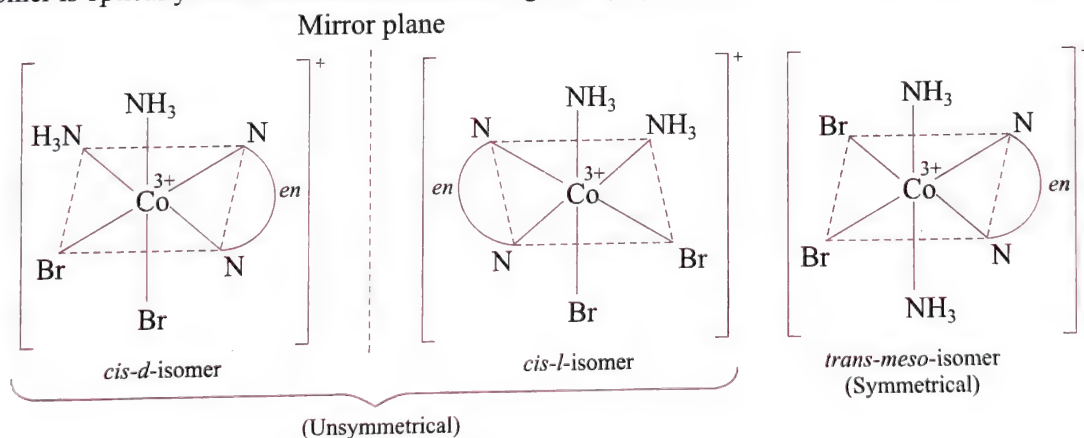


Fig. 7.26 Optical isomers of $[Co^{3+}(en)(NH_3)_2Br_2]^{\oplus}$ ion

$[Co^{3+}(C_2O_4)(NH_3)_2(NO_2)_2]^{-}$ ion is another important example of $[M(AA)a_2b_2]$ type octahedral complexes whose *cis*-isomer gives *d*- and *l*-isomers.

10. **$[M(AB)_3]$ type complexes:** We have seen that an octahedral complex of this type exists in *cis*- and *trans*-isomers (geometrical isomers). Each of these forms is optically active and hence each gives a pair of optical isomers (*d*- and *l*-forms) as shown in Fig. 7.27 for $[Cr^{3+}(gly)_3]$ complex compound.

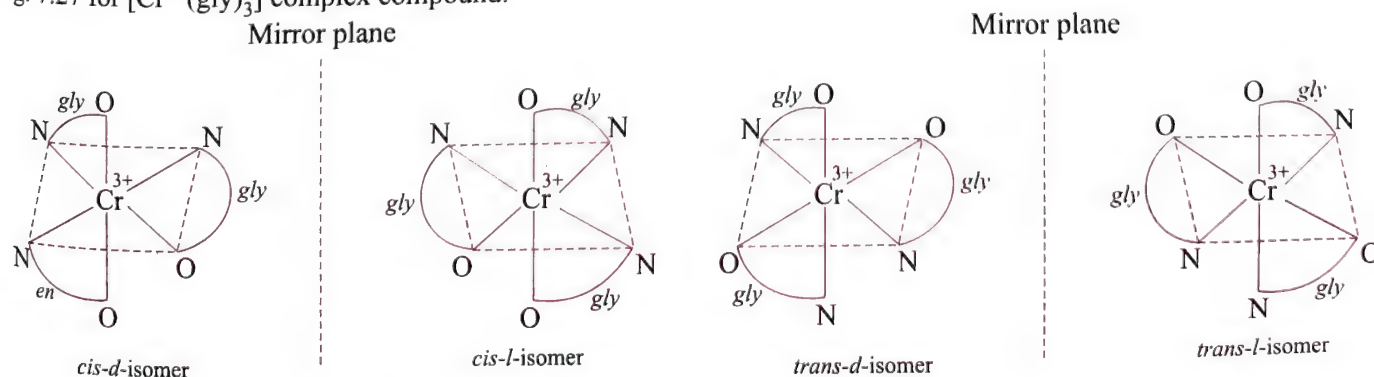


Fig. 7.27 Each of *cis*- and *trans*-isomers of $[Cr^{3+}(gly)_3]^0$ has *d* and *l* optical isomers

Table 7.14 Summary of Geometrical and optical isomerism shown by octahedral complexes (C.N. = 6)

Types of octahedral complex	Examples	Geometrical isomerism	Optical isomerism
1. $[Ma_6]$	—	×	×
2. $[Ma_5b]$	—	×	×
3. $[Ma_4b_2]$	$[Cr^{3+}(NH_3)Cl_2]^+$, $[Co^{3+}(NH_3)_4Cl_2]^+$ etc.	<i>cis</i> - and <i>trans</i> -isomers	×
4. $[Ma_3b_3]$	$[Co^{3+}(NH_3)_3Cl_3]^0$, $[Rh^{3+}(py)_3Cl_3]^0$ etc.	<i>cis</i> -(or <i>fac</i>) and <i>trans</i> -(or <i>mer</i>) isomers	×
5. $[Ma_4bc]$	$[Co^{3+}(NH_3)_2(H_2O)(Cl)]^{2+}$	<i>cis</i> - and <i>trans</i> -isomers	×
6. $[Ma_2b_2c_2]$	$[Pt^{4+}(NH_3)_2(py)_2Cl_2]^{2+}$	Five geometrical forms. Only three have been isolated	<i>cis-d</i> -isomer, <i>cis-l</i> -isomer (optical forms), <i>trans-meso</i> form
7. $[Mabcdef]$	$[Pt^{3+}(NH_3)(Cl)(Br)(I)(NO_2)(py)]^0$	15 different geometrical isomers	Each geometrical isomer has <i>d</i> - and <i>l</i> -isomers. Thus we have 30 optical isomers
8. $[M(AA)_3]$	$[Co^{3+}(en)_3]^{3+}$ etc.	×	<i>d</i> - and <i>l</i> -isomers
9. $[M(AA)_2a_2]$	$[Co^{3+}(en)_3Cl_2]^+$ etc.	<i>cis</i> - and <i>trans</i> -isomers (<i>cis</i> -isomers is unsymmetrical)	Being unsymmetrical, <i>cis</i> -isomer gives <i>cis-d</i> - and <i>cis-l</i> -isomers (optical isomers)
10. $[M(AA)_2ab]$	$[Co^{3+}(en)_2(NH_3)(Cl)]^{2+}$ etc.	<i>cis</i> - and <i>trans</i> -isomers	Being unsymmetrical, <i>cis</i> -isomer gives <i>cis-d</i> and <i>cis-l</i> -isomers (optical isomers)
11. $[M(AA)_2b_2]$	$[Co^{3+}(en)(NH_3)_2Cl_2]^+$ etc.	<i>cis</i> - and <i>trans</i> -isomers	<i>cis</i> -isomer exists as <i>cis-d</i> - and <i>cis-l</i> -isomer (optical isomers)
12. $[M(AB)_3]$	$[Cr^{3+}(gly)_3]^0$	<i>cis</i> - and <i>trans</i> -isomers (Each form is optically active)	Each geometrical form is optically active. Hence <i>cis</i> -form gives <i>cis-d</i> - and <i>cis-l</i> -optical isomers. Similarly <i>trans</i> -form gives <i>trans-d</i> - and <i>trans-l</i> -optical isomers.

Table 7.15 Summary of geometrical and optical isomerism shown by tetrahedral and square planar complexes (C.N. = 4)

Types of complexes	Geometrical isomerism	Optical isomerism
(A) Tetrahedral complexes		
1. $[Ma_4]$	×	×
2. $[Ma_3b]$	×	×
3. $[Mabcd]$ e.g. $[As^{3+}(CH_3)(C_2H_5)(S)(C_6H_4COO)]^{2-}$	×	Two optical isomer
4. Complexes of Be(II), B(III) etc. containing unsymmetrical bi-dentate ligands e.g. $[Br^{2+}(C_6H_5CO.CH_3CO)_2]^0$ and $[B^{3+}(C_6H_4OCHO)_2]^+$	×	<i>d</i> - and <i>l</i> -isomer
(B) Square planar complexes		
1. $[Ma_4]$	×	Square planar complexes rarely show optical isomerism
2. $[Ma_3b]$	×	
3. $[Mab_3]$	×	
4. $[Ma_2b_2]$ e.g. $[Pt^{2+}(NH_3)_2Cl_2]^0$	<i>cis</i> - and <i>trans</i> -isomers	
5. $[Mabcd]$ e.g. $[Pt^{2+}(NH_3)(py)(Cl)(Br)]^0$	Three isomeric forms	
6. $[Ma_2bc]$ e.g. $[Pd^{2+}Cl_2BrI]^{2-}$, $[Pt^{2+}(py)_2(NH_3)(Cl)]^+$	<i>cis</i> - and <i>trans</i> -isomers	
7. $M(AB)_2$ e.g. $[Pt^{2+}(gly)_2]^0$ (gly ⁻ ion is $NH_2CH_2COO^-$)	<i>cis</i> - and <i>trans</i> -isomers	

Note:

- Characteristics of square planar complexes
 - These have plane of symmetry.
 - These are optically inactive.
- Characteristics of tetrahedral complexes.
 - These do not have any plane of symmetry i.e., these are asymmetric.
 - These are optically active.
- cis*-isomers (geometrical isomer) is asymmetrical and hence is optically active. Being optically active, *cis*-isomer has *d-cis* and *l-cis* isomers (optical isomers).
- trans*-isomer (geometrical isomer) is symmetrical and hence is optically inactive. Being optically inactive, *trans*-isomer is *trans-meso* form.

ILLUSTRATION 7.18

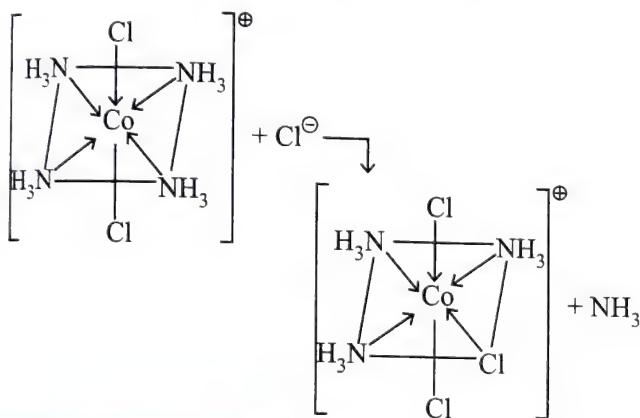
Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with central metal ion?

Sol. Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.

ILLUSTRATION 7.19

In the reaction, $[\text{CoCl}_2(\text{NH}_3)_4]^+ + \text{Cl}^- \longrightarrow [\text{CoCl}_3(\text{NH}_3)_3] + \text{NH}_3$, only one isomer of the complex product is obtained. Is the initial complex cis or trans?

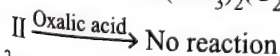
Sol. In the original complex, two Cl^- ions are present in the trans position, so that all four NH_3 molecules are equivalent and replacement of any one of them gives same product.


ILLUSTRATION 7.20

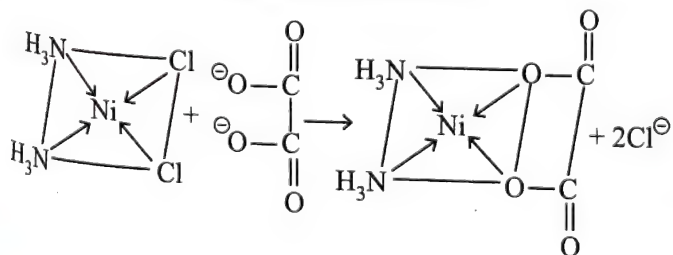
When $[\text{Ni}(\text{NH}_3)_4]^{2+}$ is treated with conc. HCl , two compounds having the formula $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$ (designated as I and II are formed). I can be converted into II by boiling in dil. HCl . A solution of I reacts with oxalic acid to form $\text{Ni}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$. II does not react with oxalic acid. Deduce the configuration of I and II and the geometry of $\text{Ni}(\text{II})$ complexes.



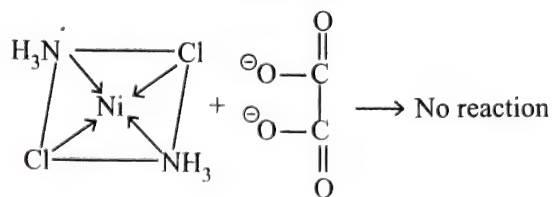
conc. (I and II)



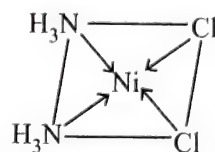
$\text{C}_2\text{O}_4^{2-}$ ion is acting as a bidentate ligand, and forms chelate ring, since I isomer of $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$ form $\text{Ni}(\text{NH}_3)_2\text{C}_2\text{O}_4$ this indicates that two Cl^- ions in I are present at cis-position.



II isomer of $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$ does not react with $\text{C}_2\text{O}_4^{2-}$ ion means that the 2 Cl^- are present at trans position.

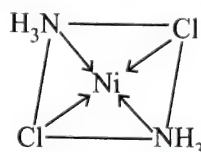


Hence I is



cis-diamminedichloridonickel(II)

and II is



trans-diamminedichloridonickel(II)

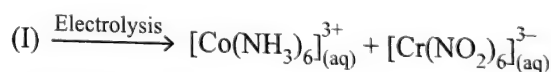
ILLUSTRATION 7.21

How can the following pair of isomers be distinguished from one another?

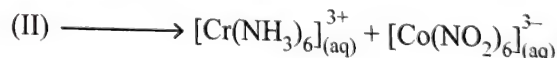
- I. $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NO}_2)_6]$ and
II. $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$
- I. $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{NO}_2)_6]$ and
II. $[\text{Cr}(\text{NH}_3)_4(\text{NO}_2)_2][\text{Cr}(\text{NH}_3)_2(\text{NO}_2)_4]$

Sol.

- I can be distinguished from II by electrolysis of their aqueous solution.



$[\text{Co}(\text{NH}_3)_6]^{3+}$ will migrate towards anode and is deposited on anode.



On electrolysis, $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ion will move towards anode and is deposited on anode.

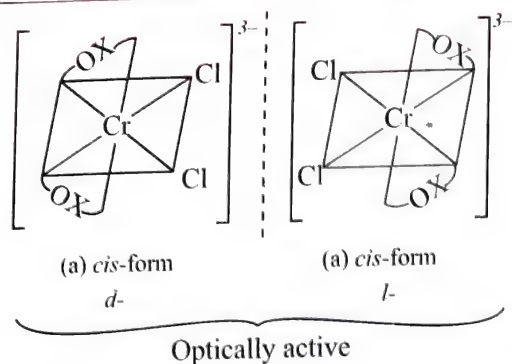
- (I) and (II) can be distinguished by conducting measurements (I) will show conductivity as (3+, 3-) electrolyte whereas (II) will conduct electricity as (+1, -1) electrolyte.

ILLUSTRATION 7.22

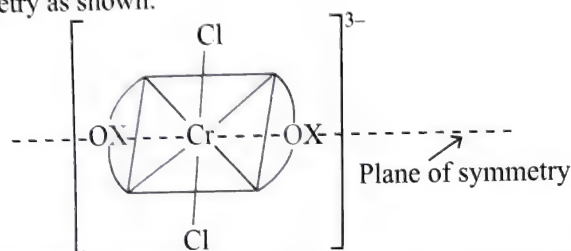
Out of the following two coordination entities which is chiral (optically active)?

- cis- $[\text{CrCl}_2(\text{OX})_2]^{3-}$
- trans- $[\text{CrCl}_2(\text{OX})_2]^{3-}$

Sol. The two geometrical isomers (a) and (b) are of the type $[\text{M}(\text{AA})_2\text{b}_2]^{n\pm}$, so (a) **cis-isomer** is chiral (optically active). The two entities are represented as:

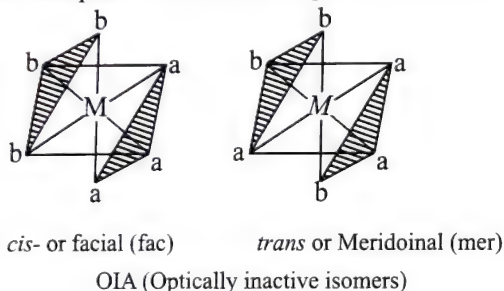


Trans-form is optically inactive, due to the presence of plane of symmetry as shown:



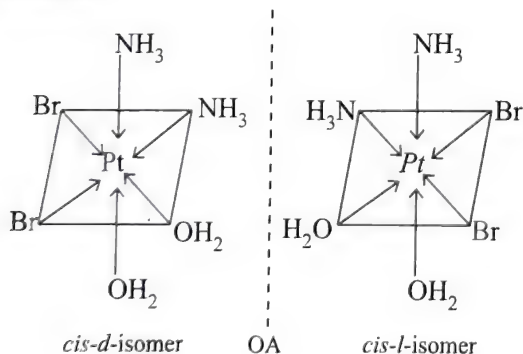
11. $[Ma_3b_3]^{n\pm}$, e.g. $[CoCl_3(NH_3)_3]$

Such complexes do not show optical isomerism.



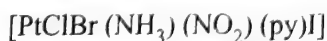
12. $[Ma_2b_2c_2]^{n\pm}$, e.g. $[Pt(NH_3)(H_2O)_2Br_2]^{2+}$

cis-isomer



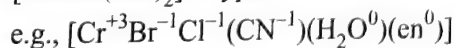
Optically active due to non-superimposable mirror image.

13. $[Mabcdef]^{n\pm}$: If the central atom is asymmetrically coordinated, each of its 15 geometrical isomers should be resolved into optical isomers, e.g.



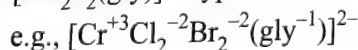
Only 3 isomers have been prepared till now, no form has been resolved.

14. $[Mabcd(AA)_2]^{n\pm}$ type



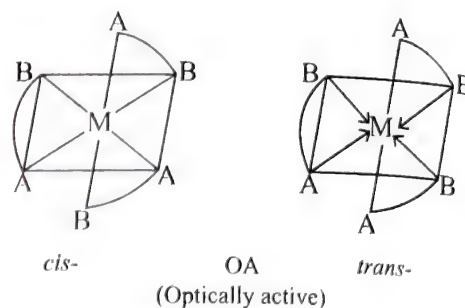
shows 12 optically active isomers.

15. $[Ma_2b_2(gly)]^{n\pm}$ type



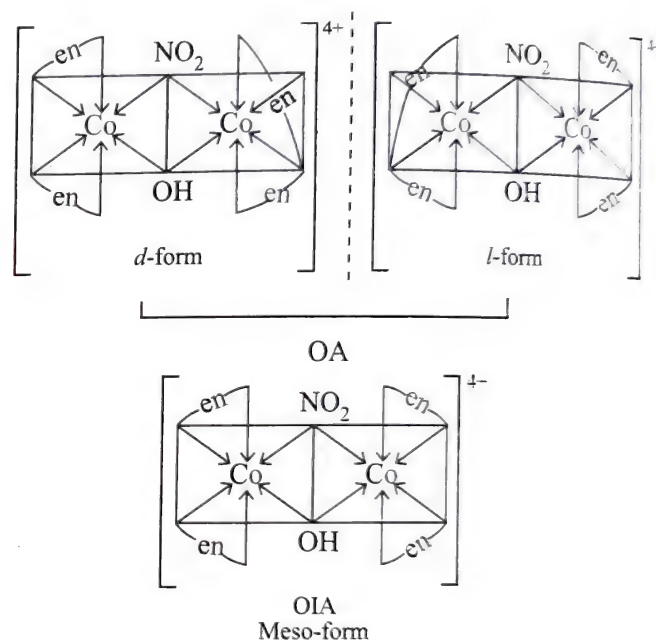
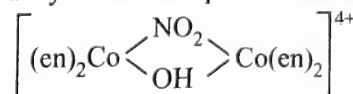
shows 4 optically active isomers.

16. $[M(AB)_3]^{n\pm}$: AB is unsymmetrical bidentate ligand, e.g. $[Cr(gly)_3]$

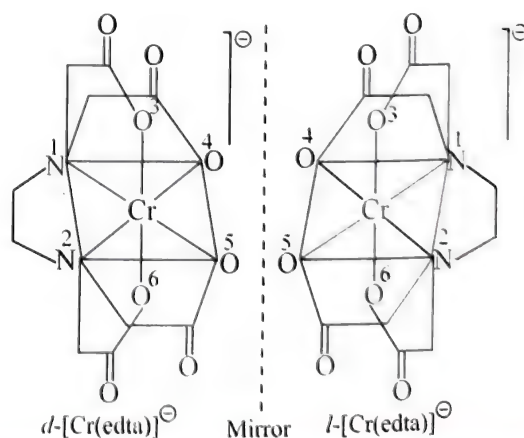


Both forms are optically active.

17. Polynuclear complexes also show optical activity, e.g.



18. Octahedral complexes containing hexadentate ligands, e.g. $[Cr(edta)]^{\ominus}$, i.e., ethylene diaminetetraacetato chromate(III) ion, also shows optical isomerism.



Note: The total number of N–Cr–O bond angles in $[Cr(edta)]^{\ominus}$ complex ion is 8, as shown below.

There are 2N-atom (N^1 and N^2) and 4O-atom (O^3, O^4, O^5, O^6). So total 8 N–Cr–O bond angle are possible as given below:

1. N^1 –Cr– O^3
2. N^1 –Cr– O^4
3. N^1 –Cr– O^5
4. N^1 –Cr– O^6
5. N^2 –Cr– O^3
6. N^2 –Cr– O^4
7. N^2 –Cr– O^5
8. N^2 –Cr– O^6

Moreover, (N–Cr–N) bond angle = 1
(O–Cr–O) bond angle = 6.

ILLUSTRATION 7.23

Write the structure and name of the following and their coordination isomers.

- (A) $[\text{Co}(\text{en})_3] [\text{Cr}(\text{CN})_6]$
- (B) $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{C}_2\text{O}_4)_3]$

Sol.

- The coordination isomer of (A) is $[\text{Cr}(\text{en})_3] [\text{Co}(\text{CN})_6]$.
The structure and name of the above two isomers are given below:

(A) \Rightarrow Tris (ethylenediamine)cobalt(III)

hexacyanochromate (III) and its isomer

Tris (ethylenediamine) chromium(III) hexacyanocobaltate (III)

- Coordination isomer of (B) is $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{C}_2\text{O}_4)_3]$. The structure and name of these isomers are given below:

(B) \Rightarrow Hexamminecobalt(III) tris (oxalato)chromate(III) and its isomer.

$[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{C}_2\text{O}_4)_3]$ is

Hexamminechromium(III) tris (oxalato)cobaltate(III).

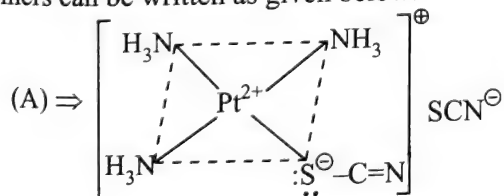
ILLUSTRATION 7.24

Draw the structures and write the names of all possible linkage isomers of:

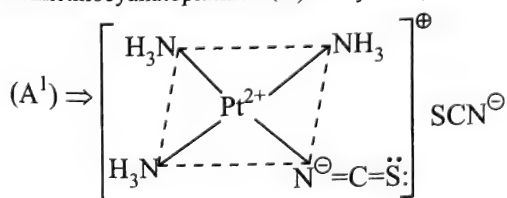
- (A) $[\text{Pt}(\text{SCN})(\text{NH}_3)_3] \text{SCN}^-$
- (B) $[\text{Co}(\text{SCN})(\text{NH}_3)_5] \text{Cl}_2$
- (C) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$

Sol.

- (A) has one linkage isomer A^1 which is $[\text{Pt}(\text{NCS})(\text{NH}_3)_3] \text{SCN}^-$. In (A^1) , SCN^- ion (ligand) is linked with Pt^{2+} ion (central metal ion) through negatively-charged N-atom. Thus the structures and names of these linkage isomers can be written as given below:



(Triammineisothiocyanatoplatinum (II) thiocyanate,



(Triammineisothiocyanatoplatinum (II) thiocyanate,

$[\text{Pt}(\text{NCS})(\text{NH}_3)_3] \text{SCN}^-$

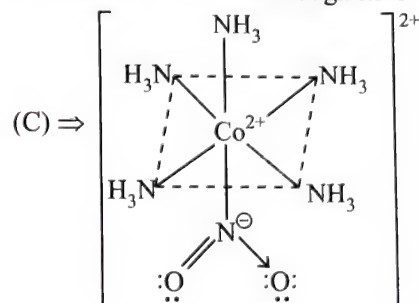
- $[\text{Co}(\text{NCS})(\text{NH}_3)_5] \text{Cl}_2$

(Pentaammineisothiocyanato cobalt (III) chloride)

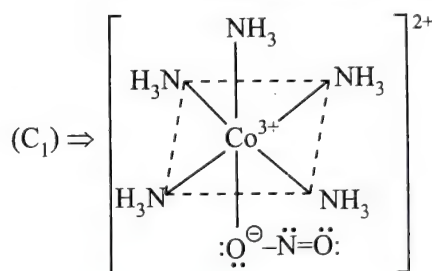
is the linkage isomer of $[\text{Co}(\text{SCN})(\text{NH}_3)_5] \text{Cl}_2$

Pentaamminethiocyanato cobalt (III) chloride

- Since NO_2^- ion is an ambidentate ligand, the given complex ion has two linkage isomers. The structures of these isomers are shown in figure. In (C) NO_2^- ion (ligand) is linked with the central Co^{3+} ion through its N-atom while in its isomer (C_1) it is linked with Co^{3+} ion through its O-atom.



(Pentamminenitrocobalt (III) ion)



(Pentamminenitritocobalt (III) ion)

ILLUSTRATION 7.25

The complex ion $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{X})$ undergoes a substitution reaction when reacted with $(\text{NaNO}_2 + \text{HCl})$. An unstable scarlet red complex A is formed when dilute acid is used and a stable yellow complex B is formed when concentrated acid is used. Both A and B are isomeric pentammine complex ions. Give the structures of the ions and name the type of isomerism involved.

Sol. Since the treatment of (X) ($\text{NaNO}_2 + \text{dil. HCl}$) gives an unstable red complex, this red complex should be pentaammine nitritocobalt (III) ion, $[\text{Co}^{3+}(\text{NH}_3)_5(\text{ONO})]^{2+}$.

Similarly, the ion obtained by treating $[\text{Co}^{3+}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{X})$ ion with $(\text{NaNO}_2 + \text{conc. HCl})$ should be pentaammine nitrocobalt (III) ion, $[\text{Co}^{3+}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$.

Thus $A = [\text{Co}^{3+}(\text{NH}_3)_5(\text{ONO})]^{2+}$ and

$B = [\text{Co}^{3+}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$.

Obviously A and B linkage isomers and the isomerism involved is linkage isomerism.

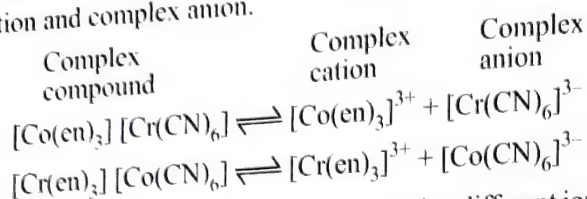
ILLUSTRATION 7.26

What type of isomers are the following:

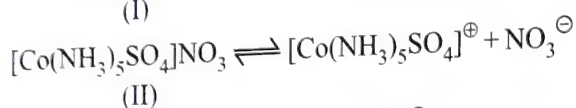
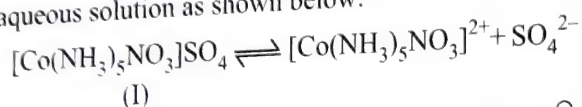
- $[\text{Mn}(\text{CO})_5(\text{SCN})]$ and $[\text{Mn}(\text{CO})_5(\text{NCS})]$
 - $[\text{Co}(\text{en})_3] [\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{en})_3] [\text{Co}(\text{CN})_6]$
 - $[\text{Co}(\text{NH}_3)_5\text{NO}_3] \text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4] \text{NO}_3$
 - $[\text{Co}(\text{py})_2(\text{H}_2\text{O})_2\text{Cl}_2] \text{Cl}$ and $[\text{Co}(\text{py})_2(\text{H}_2\text{O})\text{Cl}_3] \cdot \text{H}_2\text{O}$
- $[\text{Cr}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_4(\text{CN})_2] [\text{Cr}(\text{NH}_3)_2(\text{CN})_4]$
 - $[\text{Pt}(\text{NH}_3)_4\text{Br}_2] \text{Cl}_2$ and $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2] \text{Br}_2$

Sol.

- I. a. The given complexes are **linkage isomers**, since these complexes have ambidentate ligand viz. SCN^\ominus ion.
- b. The given complex compounds are **coordination isomers**, since each of them contains complex cation and complex anion as shown below and these complex compounds can be obtained by interchanging the ligands present in complex cation and complex anion.

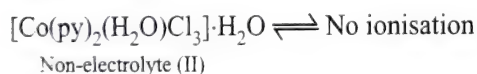
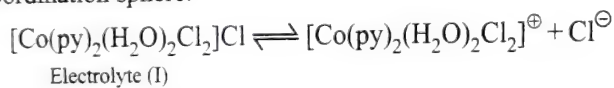


- c. These are **ionisation isomers**, since they give different ions in aqueous solution as shown below:

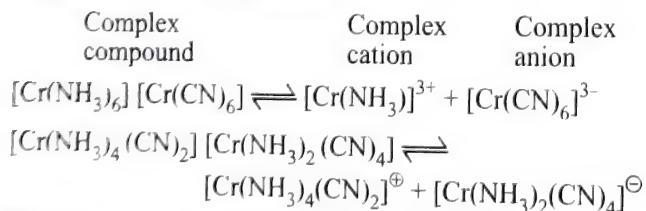


(I) gives SO_4^{2-} ions and (II) gives NO_3^\ominus ions. Complex cations given by them are also different. Due to the production of SO_4^{2-} ions, (I) gives a white precipitate of BaSO_4 with BaCl_2 solution. On the other hand, (II) gives the test of NO_3^\ominus ions.

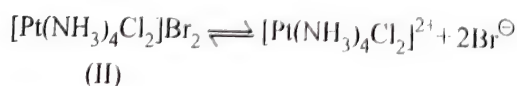
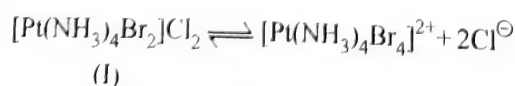
- d. These compounds are **hydrate isomers**, since they contain different number of H_2O molecules inside and outside coordination sphere.



- II. a. The given complex compounds are **coordination isomers**, since each of them contains complex cation and complex anion as shown below and these isomers can be obtained by interchanging their ligands.



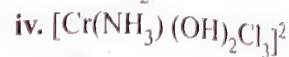
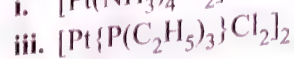
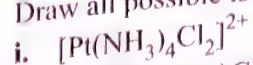
- b. The given complex compounds are **ionisation isomers**, since they give different ions in aqueous solution as shown below:



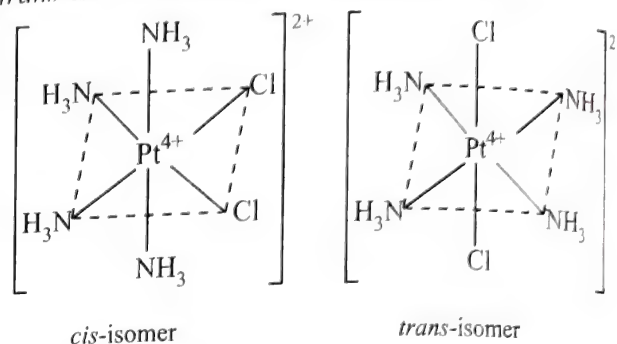
(I) gives Cl^\ominus ions and (II) gives Br^\ominus ions. (I) gives white precipitate of AgCl with AgNO_3 solution. On the other hand, (II) gives yellow precipitate of AgBr with AgNO_3 solution.

ILLUSTRATION 7.27

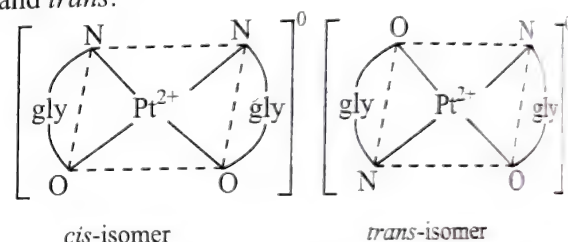
Draw all possible isomers of:

**Sol.**

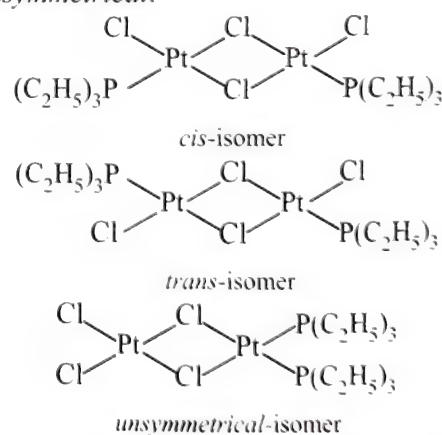
- i. $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$ ion: This ion is an octahedral ion of $[\text{Ma}_4\text{b}_2]$ type and hence has two geometrical isomers viz *cis* and *trans* isomers. In *cis*-isomer two Cl^\ominus ions are in *cis*-position and in *trans*-isomer these ions have *trans* position.



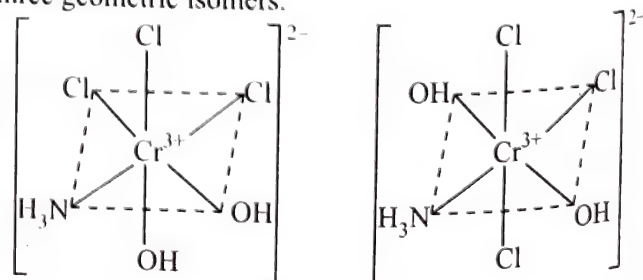
- ii. $[\text{Pt}(\text{gly})_2]^0$: It is a square planar complex of $[\text{M}(\text{AB})_2]$ type in which gly^\ominus ion ($\text{NH}_2\text{CH}_2\text{COO}^\ominus$) is an unsymmetrical bidentate ligand. This complex has two geometrical isomers viz *cis* and *trans*.

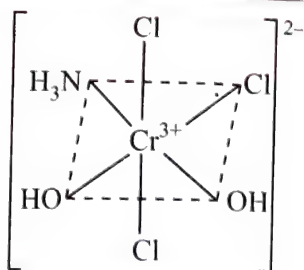


- iii. $[\text{Pt}\{\text{P}(\text{C}_2\text{H}_5)_3\}\text{Cl}_2]_2$: It is a bridged binuclear planar complex and exists in three isomeric forms viz *cis*, *trans* and *unsymmetrical*.



- iv. $[\text{Cr}(\text{NH}_3)(\text{OH})_2\text{Cl}_3]^{2+}$ ion: $[\text{Ma}_3\text{b}_2\text{c}]^{n\pm}$ type. This ion has three geometric isomers.





c. Cl-Cl trans, OH-OH cis

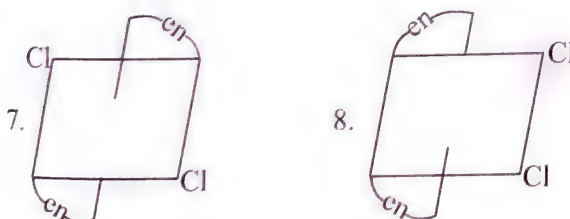
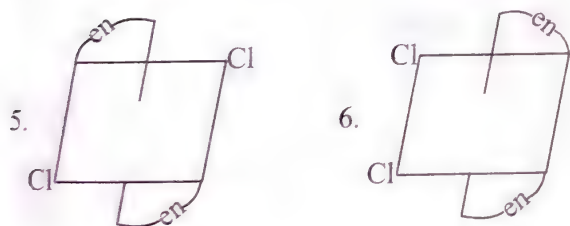
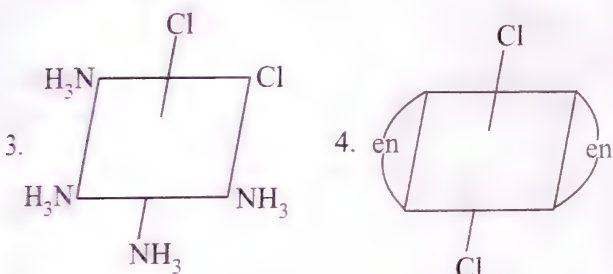
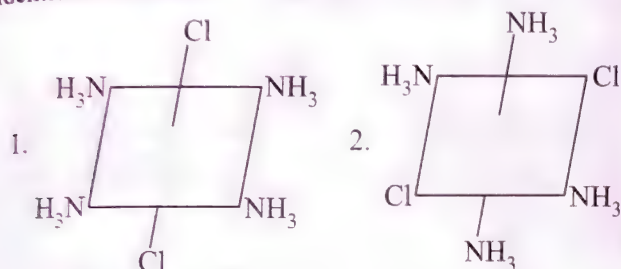
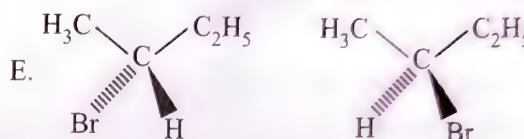
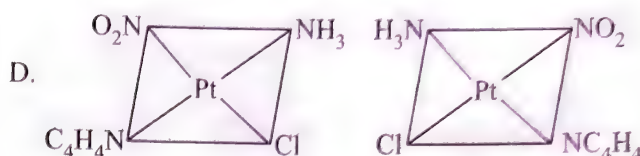
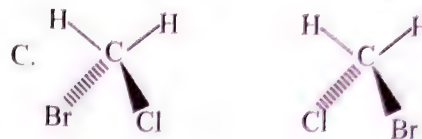
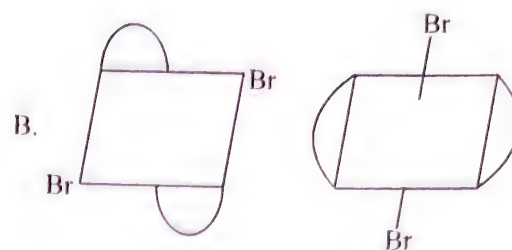
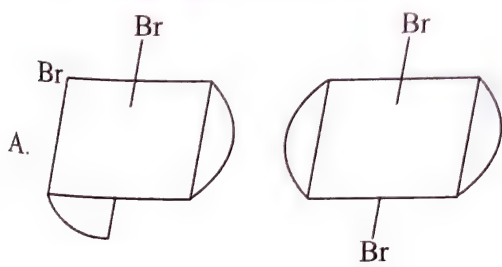
ILLUSTRATION 7.28

I. Neither optical nor geometrical isomers can be distinguished by mass spectroscopy. Why?

II. Select the pairs of

a. Geometrical isomers b. Optical isomers

c. Identical structures.


 II. Identify the type of isomerism in:
(If no isomerism then indicate none)

Sol.

I. Since all atoms in each isomers are attached to the same other types of atoms, the same fragments are expected when the molecules are split.

Therefore ultraviolet (UV), nuclear magnetic resonance (NMR) and X-ray diffraction, conductance method, electrolysis method, chemical method, dipole magnetic and magnetic properties method are used to distinguish isomers.

II. a. Geometrical isomers are 1 and 3,

4 with 6 and 8

7 with 6 and 8

5 with 6 and 8.

b. Optical isomers are 6 and 8.

c. Identical structures are 1 and 2,

4, 5 and 7.

III. A. Geometrical isomers

B. None

C. None

D. None

E. Optical active isomers

ILLUSTRATION 7.29

Predict the total number structural and stereoisomers of the following:

 I. $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$

 II. $[\text{Ru}(\text{H}_2\text{O})_4\text{Br}_2]^{\oplus}$

 III. $[\text{Co}(\text{en})_2\text{I}_2]^{\oplus}$

 IV. $[\text{Ir}(\text{py})_2\text{H}(\text{Cu})]^{2+}$

 V. $[\text{Co}(\text{Br})(\text{Cl})(\text{en})_2]$

 VI. $\text{Na}_3[\text{CoBr}_2(\text{OX})_2]$

 VII. $\text{Na}_3[\text{Cr}(\text{OX})_3]$

 VIII. $[\text{Cr}(\text{CN})_3(\text{NH}_3)_3]$

Sol.

- I. $[Ma_3b]^{n\pm}$ type:
Structural isomers = 0
Geometrical isomers = 0
Optical isomers = 0
- II. $[Ma_4b_2]^{n\pm}$ type:
Structural isomers = 0
Geometrical isomers = 2
Optical isomers = 0
- III. $[M(AA)_2b_2]^{n\pm}$ type:
Structural isomers = 0
Geometrical isomers = 2 [*cis* \Rightarrow *d* and *l* *trans* \Rightarrow *meso*]
Optical isomers = 3
Total stereoisomers = 3
- IV. $[Ma_2bc]^{n\pm}$ types, (square planar)
Structural isomers = 0
Geometrical isomers = 2
Optical isomers = 2
Total stereoisomers = 2
- V. $[M(AA)_2bc]^{n\pm}$ type:
Structural isomers = 0
Geometrical isomers = 2 (*cis* \Rightarrow *d* and *l* *trans* \Rightarrow *meso*)
Optical isomers = 3
Total stereoisomers = 3.
- VI. $[M(AA)_2b_2]^{n\pm}$ type:
Structural isomers = 0
Geometrical isomers = 2 (*cis* \Rightarrow *d* and *l* *trans* \Rightarrow *meso*)
Optical isomers = 3
Total stereoisomers = 3.
- VII. $[M(AA)_3]^{n\pm}$ type:
Structural isomers = 0
Geometrical isomers = 0
Optical isomers = 0

ILLUSTRATION 7.30

Predict the number of stereoisomers of the following compounds/ions.

- I. $[CrCl_2(H_2O)(NH_3)_3]$ II. $[Pt FCl(CN)(H_2O)]^y$
III. $[Pt(gly)_2]$ IV. $[Cr(en)(H_2O)_4]^{3+}$

Sol.

- I. No. of stereoisomers = 3, *cis* = 1, *trans* = 2.
II. No. of stereoisomers = 3, All geometrical isomers.
III. No. of stereoisomers = 2, Both are in *d* and *l* forms
IV. No. of stereoisomers = 0.

ILLUSTRATION 7.31

Predict the type of isomerism of the following compounds.

- I. $[Cr(CN)(NH_3)_3(en)(C_2O_4)]$ II. $[Cr(ox)(H_2O)_3(NH_3)] ClO_4^y$

- III. $[Zn Cl Br (CN)(NH_3)_3]^y$ IV. $[Cr(BrCl)(H_2O)_4] [Ag(CN)_2]$
V. $[Cr Br_2 (H_2O)_2 (NH_3)_2] Cl$

Sol.

- I. It can exhibit linkage and geometrical isomerism.
II. It can exhibit geometrical isomerism. Does not exhibit structural and optical isomerism.
III. It exhibits optical isomerism
IV. $[Cr(BrCl)(H_2O)_4] [Ag(CN)_2]$ and $[CrCl(CN)(H_2O)_4] [AgBr(CN)]$ are coordination isomers.
V. It exhibits ionization, geometrical and optical isomerism.

Note: $[Cr Br_2 Cl (H_2O)(NH_3)_2]$, H_2O is not hydrate isomer of the complex (V)

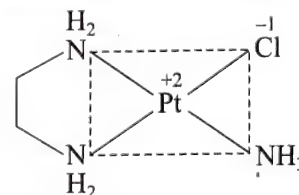
ILLUSTRATION 7.32

Predict the number of stereoisomer's of the following compounds/ions.

- I. $[PtCl(NH_3)(en)]$ II. $[Cr(acac)_3]$
III. $Zn(CN)(NH_3)(gly)$ IV. $[PdClF(CN)(NH_3)]^\ominus$

Sol.

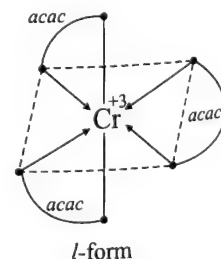
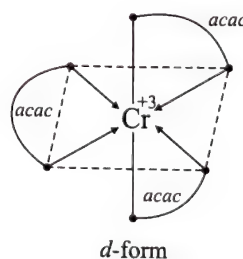
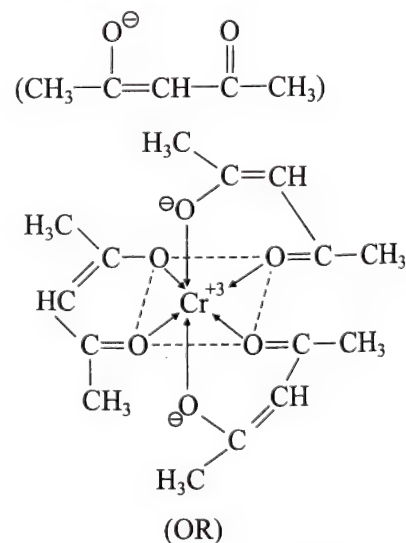
- I. It does not exhibit geometrical and optical isomerism because it contains plane of symmetry.



- II. It exhibits optical isomerism.

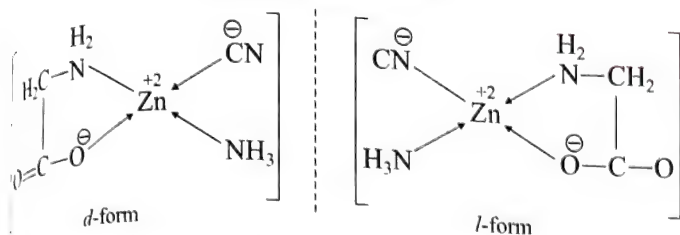
Number of stereoisomers = 2

$(acac)^\ominus \Rightarrow$ Acetyl acetonato ion



III. It exhibits optical isomerism.

Number of Stereoisomers-2



IV. Hybridisation of Pd^{2+} is dsp^2 . Complex has plane of symmetry hence does not exhibit optical isomerism. But it exhibits geometrical isomerism and number of geometrical isomers = 3.

ILLUSTRATION 7.33

Predict the number of stereoisomers of the following compounds/ions.

- I. $[\text{PtCl}_2(\text{H}_2\text{O})_2]$
- II. $[\text{CoCl}(\text{CN})(\text{en})_2]^{\oplus}$
- III. $[\text{Cr}(\text{en})_3]^{3+}$
- IV. $[\text{Cd}(\text{gly})(\text{H}_2\text{O})(\text{NH}_3)]^{\oplus}$
- V. $[\text{M}(\text{en})_2]$
- VI. $[\text{M}(\text{en})(\text{gly})]$
- VII. $[\text{M}(\text{gly})(\text{NH}_3)_2]$

- Sol.**
- I. $\Rightarrow 2$ stereoisomers (dsp^2)
 - II. $\Rightarrow 3$ stereoisomers (d^2sp^3)
 - III. $\Rightarrow 2$ stereoisomers (d^2sp^3)
 - IV. $\Rightarrow 2$ stereoisomers (sp^3)
 - V. VI. and VII. does not show stereoisomerism. When symmetrical bi-dentate ligand present in coordination number of 4, it does not show stereoisomerism.

ILLUSTRATION 7.34

How many geometrical and stereoisomers are possible for

- I. $[\text{Mabcd}]^{n\pm}$ and
- II. $[\text{Mabcdef}]^{n\pm}$ type compounds respectively.

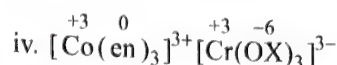
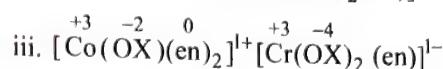
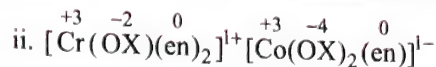
- Sol.**
- I. $[\text{Mabcd}]^{n\pm}$ type $\Rightarrow 3$ geometrical isomers no optical isomers.
 - II. $[\text{Mabcdef}]^{n\pm}$ type $\Rightarrow 15$ geometrical isomers and each isomer is optically active.
- Total number of stereoisomers for II. = $15 + 15 = 30$

ILLUSTRATION 7.35

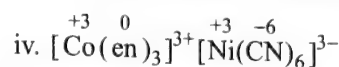
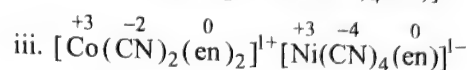
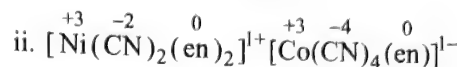
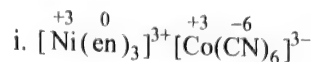
Predict the number of possible coordination isomers for the following compounds.

- a. $[\text{Cr}(\text{en})_3] [\text{Co}(\text{OX})_3]$
- II. $[\text{Ni}(\text{en})_3] [\text{Co}(\text{CN})_6]$
- III. $[\text{Cu}(\text{H}_2\text{O})_4] [\text{CuI}_4]$

- Sol.**
- I. Total coordination isomers = 4.
 - i. $[\text{Cr}(\text{en})_3]^{3+} [\text{Co}(\text{OX})_3]^{3-}$



II. Total coordination isomers = 4



III. Total coordination isomers = 2

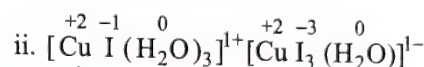
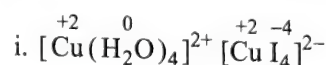
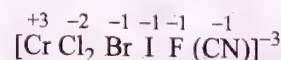


ILLUSTRATION 7.36

If x = Number of cis isomers

y = Number of trans isomers

then calculate $\frac{x}{y}$ for the complex



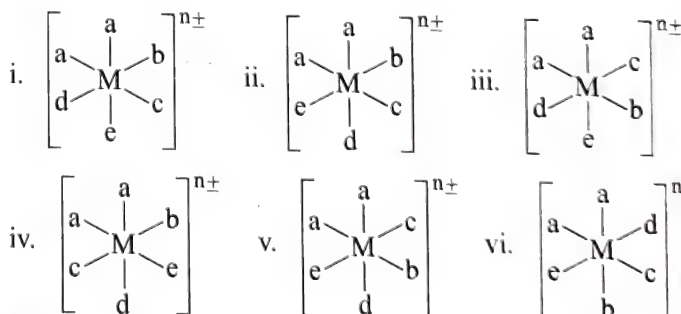
Sol. (2) For $[\text{Ma}_2\text{bcde}]^{n\pm}$ type:

x = No. of cis isomers = 6

y = No. of trans isomers = 3

$$\therefore \frac{x}{y} = \frac{6}{3} = 2$$

Cis isomers are:



Trans isomers are:

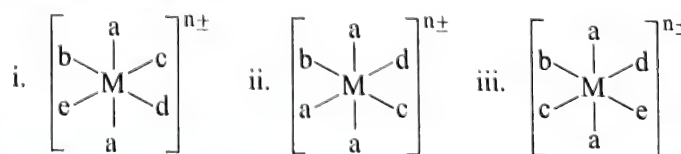
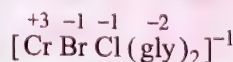
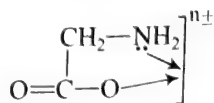


ILLUSTRATION 7.37

Predict the number of geometrical isomers for the complex.

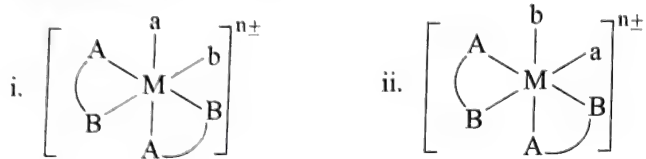


Sol. (6) For $[Mab(AB)_2]^{n\pm}$ type
(where AB is unsymmetrical bi-dentate ligand e.g.: glycinate:)



No. of geometrical isomers = 6 (2 cis + 4 trans).

Cis isomers:



Trans isomers:

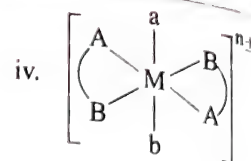
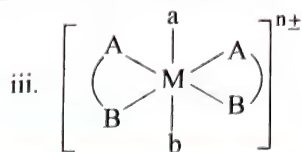
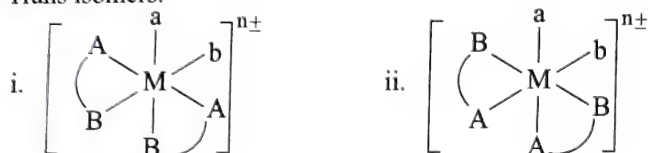
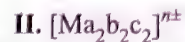
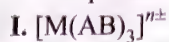


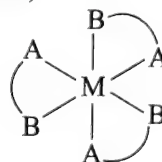
ILLUSTRATION 7.38

Predict the total number of stereoisomers of the following types of compounds.

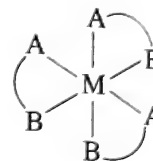


Sol.

I. No. of stereoisomers = 4 (cis and trans & both optically active)

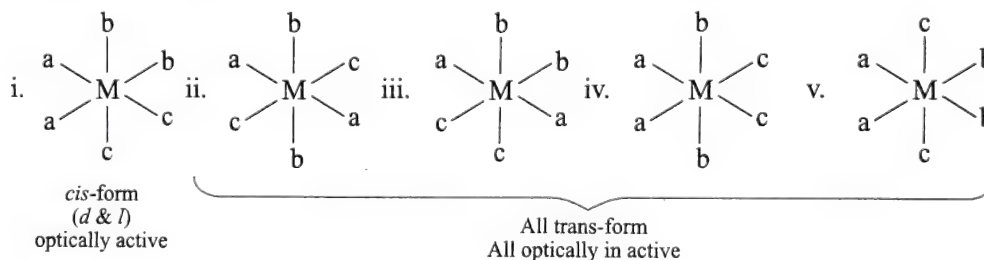


cis-form
(d & l)
optically active



trans-form
(d & l)
optically active

II. No. of stereoisomers = 6 (1 cis \Rightarrow optically active 4 trans \Rightarrow all optically inactive)



III. No. of stereoisomers = 3 (All optically inactive).

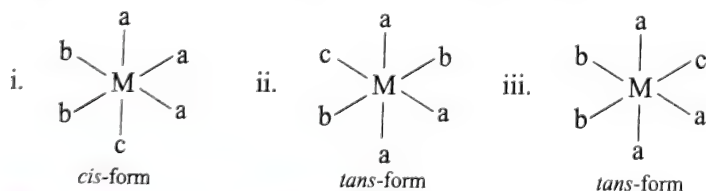
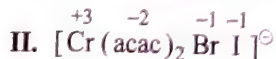


ILLUSTRATION 7.39

If x = total number of geometrical isomers in complex:



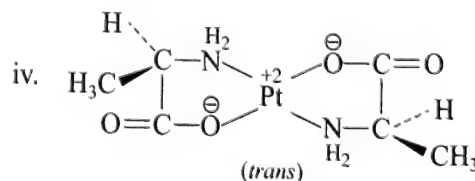
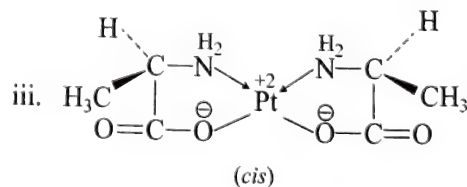
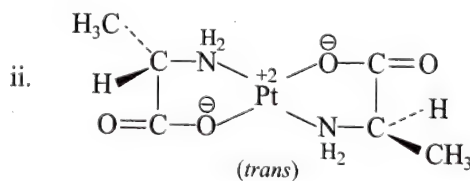
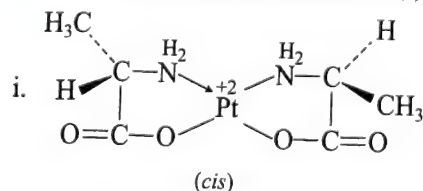
y = total number of stereoisomers in complex:



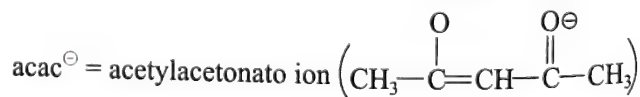
Then the value of $\frac{x}{y}$ is

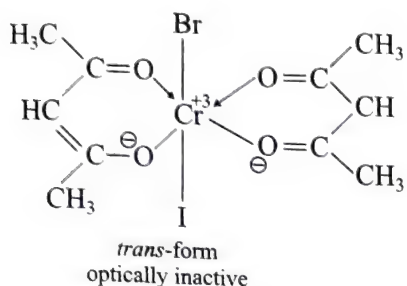
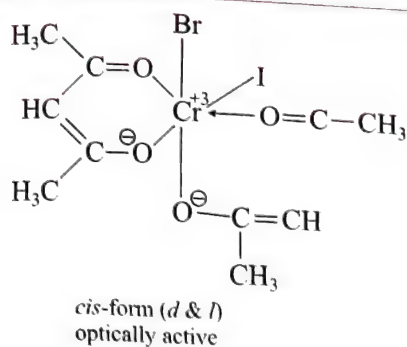
Sol. (1.33)

x = No. of Geometrical isomers in (I) = 4 (2 cis + 2 trans)



y = No. of stereoisomers in II = 3 [1 cis \Rightarrow optically active, 1 trans \Rightarrow optically inactive]





$$\therefore \frac{x}{y} = \frac{4}{3} = 1.33$$

7.9 MAGNETIC PROPERTIES OF COORDINATION COMPOUNDS

The transition metal complexes whose central atom/ion contains one or more unpaired electrons are paramagnetic while those central atom/ion which have no unpaired electrons (i.e., all electrons are paired) behave as **diamagnetic** substances. Paramagnetic character increases with increase in number of unpaired electrons. The paramagnetism of a complex is expressed in terms of magnetic moment (μ). Greater is the number of unpaired electrons in the central atom/ion of given compound, greater is its paramagnetic character and hence larger is the value of magnetic moment of the complex. The magnetic moment is expressed in terms of Bohr Magnetons (BM). Paramagnetic substances have some value of magnetic moment whereas diamagnetic substances have zero magnetic moment.

For transition metal complexes,

$$\mu = \mu_l + \mu_s$$

where μ_l = orbital magnetic moment, i.e. magnetic moment due to orbital motion of electron.

μ_s = spin magnetic moment, i.e. magnetic moment due to spin motion of electron.

$$\mu = \left[\sqrt{l(l+1)} + 2\sqrt{s(s+1)} \right] \frac{eh}{4\pi m}$$

$$= \left[\sqrt{l(l+1)} + 2\sqrt{s(s+1)} \right] \text{B.M.}$$

BM is Bohr Magnetron.

$$1\text{BM} = \frac{eh}{4\pi m}$$

where

e = charge on electron

h = Plank's constant

m = mass of electron

In case of transition metal ions of 3d-series, the crystal fields (i.e., the ligands surrounding the metal ions) restrict the movement

of the electron around the nucleus in orbitals and hence magnetic moment due to orbital motion of the electron is quenched ($\mu_l = 0$) and hence $\sqrt{l(l+1)} = 0$. Thus magnetic moment of an unpaired electron residing in 3d-orbital of ions of 3d-series is

$$\mu = 2\sqrt{s(s+1)} \text{ BM}$$

$$\therefore s = \frac{1}{2} \text{ (for one electron)}$$

$$\mu = 2\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} \text{ BM}$$

For n unpaired electrons, μ_{eff} is given as

$$\mu_{\text{eff}} = 2\sqrt{\frac{n}{2}\left(\frac{n}{2}+1\right)} \text{ BM}$$

Since μ_{eff} is only due to the spin motion of n unpaired electrons it is also called spin only magnetic moment and is represented as μ_s .

$$\mu_{\text{eff}} = \mu_s = \sqrt{n(n+2)} \text{ BM}$$

The above equation shows that value of μ_{eff} depends only on the number of unpaired electrons present in the species.

Greater is the number of unpaired electrons present in orbitals of central metal atom/ion, greater is the value of μ_{eff} as shown below:

Number of unpaired electrons	Magnetic moment (μ_s) in Bohr magnetons
0	0
1	$\sqrt{3} = 1.73$
2	$\sqrt{8} = 2.83$
3	$\sqrt{15} = 3.83$
4	$\sqrt{24} = 4.90$
5	$\sqrt{35} = 5.92$

CONCEPT APPLICATION EXERCISE 7.1

Terminology

1. Write the formula of the following compounds according to the IUPAC rule.

- Potassium tetraxoferrate(IV)
- Potassium tetrazidocobalt(II)
- Dichloridobis (triphenylphosphine) nickel(II)
- Chloridocarbonylbis (triphenyl phosphine) iridium(I)
- Hexammine cobalt(III) pentachloridocuprate(II)
- Tetrammine- μ -dihydroxobis (ethylenediamine) dicobalt(III) chloride.
- Dibromidotetra ammine cobalt (III) tetrachloridozincate(II)
- Hexammine nickel(II) hexanitrocobaltate(III)
- Hexammine cobalt(III) tetrachloridodiammine chromate(III).

2. Name the following compounds:

- $[\text{FeCl}_2(\text{H}_2\text{O})_4]^{\oplus}$
- $[\text{Cr}(\text{en})_2\text{Cl}_2] \text{Cl}$
- $[\text{Pt}(\text{Py})_4] [\text{PtCl}_4]$
- $[\text{Co}(\text{en})_2(\text{CN})_2]\text{ClO}_3$

- e. CsTeF_5 f. $[\text{Co}(\text{NH}_3)_5\text{CO}_3]_2 [\text{CuCl}_4]$
 g. $\text{NaMn}(\text{CO})_5$ h. $(\text{NH}_4)_2\text{TiCl}_6$
 i. $\left[\begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ (\text{en})_2\text{Co} \quad \text{Co}(\text{en})_2 \\ \diagdown \quad \diagup \\ \text{OH} \end{array} \right]^{3+}$
 j. $[\text{Cr}(\text{acac})_3]$ k. $[\text{Ni}(\text{dmg})_2]$
 l. $\text{SnCl}_4 (\text{Et}_2\text{NH})_2$

3. Give the characteristic coordination number of each of the following central metal ions:

- a. Cu(I) b. Cu(II)
 c. Co(III) d. Al(III)
 e. Zn(II) f. Fe(II)
 g. Fe(III) h. Ag(I)

4. Indicate the oxidation state of the central metal ion in each of the following complex.

- a. $[\text{Cu}(\text{NH}_3)_4]^{2+}$ b. $[\text{Cu}(\text{Br}_4)]^{2-}$
 c. $[\text{Cu}(\text{CN})_2]^\ominus$ d. $[\text{Cr}(\text{NH}_3)_4\text{CO}_3]^\oplus$
 e. $[\text{PtCl}_4]^{2-}$ f. $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^\ominus$
 g. $\text{Fe}(\text{CO})_5$ h. $[\text{ZnCl}_4]^{2-}$
 i. $[\text{Fe}(\text{en})_3]^{2+}$

5. Calculate the freezing point of the solution containing 24.8 g solute per kg water for each of the following solutes; $K_f = 1.86^\circ\text{C/m}$

- a. $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$
 b. $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2] [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$
 c. $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)] [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$
 [Mw of (a) 248 g (b) 496 g (c) 744 g]

Effective Atomic Number (EAN)

6. Calculate EAN in

- a. $[\text{Cr}(\text{CN})_6]^{3-}$ b. $[\text{PdCl}_4]^{2-}$
 c. $[\text{Pt}(\text{NH}_3)_4]^{2+}$ d. $[\text{Cu}(\text{CN})_4]^{3-}$

7. Calculate "EAN" of metal atoms in the following:

- a. $\text{Fe}(\text{CO})_5$ b. $\text{Co}_2(\text{CO})_8$
 c. $\text{Fe}(\text{NO})_2(\text{CO})_3$ d. $\text{Fe}(\text{C}_5\text{H}_5)_2$

8. Predict the value of x in each of the following carbonyls:

- a. $\text{Co}_2(\text{CO})_x$ b. $\text{H}_x\text{Cr}(\text{CO})_5$
 c. $\text{H}_x\text{Co}(\text{CO})_4$ d. $\text{Mo}(\text{CO})_x$

9. (a) If complex compound $[\text{Fe}(\pi - \text{C}_5\text{H}_5)_x (\pi - \text{C}_3\text{H}_5)_y (\text{CO})_z]$ is following sidwick's rule of EAN then value of expression " $x + y + z$ " is

(b) If complex $[\text{Mn}(\text{CO})_x (\eta^5 - \text{C}_5\text{H}_5)]$ follows EAN rule, then value of expression " $x + y$ " is

(c) Calculate the EAN of central metal atom/ion in the following species/compound.

- (I) $[\text{Co Br I}(\text{Trien})]^\oplus$ (II) $[\text{Ni}(\text{dmg})_2]$
 (III) $[\text{Cr}(\text{en})_3]^{3+}$ (IV) $[\text{Ca}(\text{EDTA})]^{2-}$
 (V) $[\text{Ni}(\text{CO})_4]$ (VI) $[\text{Fe}(\text{CN})_6]^{4-}$

10. (a) EAN of $\text{Co}(\text{CO})_4$ is 35 and hence is less stable. How it attains stability.

(b) Which of the following is an oxidizing agent and reducing agent.

- (I) $\text{Fe}(\text{CO})_9$ (II) $\text{Mn}(\text{CO})_6$
 (III) $\text{Mn}(\text{CO})_5$ (IV) $\text{Mn}_2(\text{CO})_{10}$

Conductance in Coordination Compounds

11. Arrange the following in order of increasing conductivity in solution.

- a. $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ b. $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$
 c. $\text{Co}(\text{NH}_3)_4\text{Cl}_3$ d. K_2PtCl_6

12. Two compounds have the empirical formula $\text{Cr}(\text{NH}_3)_3(\text{NO}_2)_3$. In aqueous solution, one of these conducts electricity while the other does not. Deduce their probable structures.

Isomerism in Coordination Compounds

13. How will you distinguish between the following pairs of isomers $[\text{Cr}(\text{NH}_3)_3(\text{NO}_2)_3]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{NO}_2)_6]$.

14. How many geometrical isomers are possible for the complex ion $[\text{Cr}(\text{NH}_3)(\text{OH})_2\text{Cl}_3]^{2-}$.

15. The complex $\text{M}(\text{C}_2\text{O}_4)\text{Cl}_2(\text{NH}_3)_2$ forms two types of ionic coloured crystals viz., red (A) and blue (B). Both A and B reacts with 1 mole of AgNO_3 to give 1/2 mole of a red precipitate. Further 1 mole of A reacts slowly with 1 mole of $\text{Ag}_2\text{C}_2\text{O}_4$ to form 2 moles of a white precipitate but B does not react with $\text{Ag}_2\text{C}_2\text{O}_4$. From the above data. Find

- a. the coordination number of M
 b. the hybrid orbitals of M and
 c. stereochemistry of red and blue forms

16. The compound $\text{Co}(\text{en})_2(\text{NO}_2)_2\text{Cl}$ has been prepared in these isomeric forms A, B and C. A does not react with AgNO_3 or (en) and is optically inactive. B reacts with AgNO_3 but not with (en) and is optically inactive. C is optically active and reacts with both AgNO_3 and (en). Identify each of these isomeric forms and draw their structures.

17. A solution containing 1 g of the complex $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ was passed through a cation exchanger. The acid liberated was made up to 1 litre. Calculate the strength of acid solution. (Aw of Cr = 52 and Mw of complex = 266.5 g mol^{-1})

18. A solution containing 2.675 g of $\text{CoCl}_3 \cdot 6\text{NH}_3$ was passed through a cation exchanger. The solution obtained gave 4.305 g of AgCl precipitate with AgNO_3 solution. Determine the formula of the complex.
 (Mw of $\text{CoCl}_3 \cdot 6\text{NH}_3 = 267.5$)

7.10 BONDING IN COORDINATION COMPOUNDS: VALENCE BOND THEORY (VBT)

The theory was developed by Pauling in 1931. The basic principles involved in this theory are as follows:

- a. **Orbital hybridisation:** The model utilises the hybridisation of s , p and d valence orbitals of central metal atoms or

ions (in which electron pairs donated by the ligands are accommodated) to account for observed structures and magnetic properties.

- b. **Bonding between ligand and the metal atom or ion:** From the valence point of view, formation of complex involves reaction between Lewis bases (ligands) and Lewis acids (metal atom/ion) with the formation of coordinate covalent (or dative) bonds between them.
- c. **Relation between the observed magnetic behaviour and the bond type:** That is, the geometry of coordination entity can be predicted if its magnetic behaviour is known.

7.10.1 ASSUMPTIONS OF VBT

- The ligands have at least one σ -orbital containing a lone pair of electrons.
- Metal-ligand bond ($L \rightarrow M$) arises by the donation of pairs of electrons by ligands to the empty hybridised orbitals of central metal atom or ion. It is basically overlap of atomic orbital of both the entities.
- In order to accommodate these electrons, the metal ion must possess same number of vacant orbitals of equal energy. These orbitals of metal atom (s, p or d) undergo hybridisation to give a set of hybrid orbitals of equal energy and with definite directional properties. These vacant hybrid orbitals now overlap with the ligands to form strong coordinate bonds.
- The non-bonding electrons of the metal occupy the inner orbitals. They are grouped in accordance with Hund's rule. However, under the influence of some strong ligands, there may be some rearrangement of inner electrons in the atomic orbitals (against Hund's rule). During rearrangement generally pairing takes place and consequently some orbitals are vacated and made available for hybridisation.
- (For octahedral complexes only) The d -orbitals involved in the hybridisation may be either $(n-1) d$ -orbitals or nd -orbital (n refers to the outermost principle shell of the central metal atom). The complexes formed in two ways are referred to as inner orbital complex (or entity) or outer orbital complex (entity). On the basis of spin they are also referred as low spin and high spin complexes respectively.
- If a complex contain unpaired electrons, it is paramagnetic in nature, whereas if it does not contain unpaired electrons it is diamagnetic in nature.
- Square planar, tetrahedral and octahedral complexes are formed as a result of dsp^2 , sp^3 and d^2sp^3 (or sp^3d^2) hybridisation.

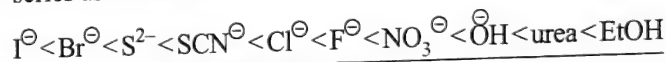
7.10.2 TYPE OF GEOMETRY (STRUCTURES) OF COMPLEX ENTITIES

In predicting the geometry of complexes, the following points are helpful:

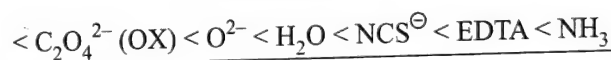
- Electronic configuration of first transition series:

Atomic number (Z)	Element	Electronic configuration
21	Sc	$3d^1 4s^2$
22	Ti	$3d^2 4s^2$
23	V	$3d^3 4s^2$
24	Cr	$3d^5 4s^1$
25	Mn	$3d^5 4s^2$
26	Fe	$3d^6 4s^2$
27	Co	$3d^7 4s^2$
28	Ni	$3d^8 4s^2$
29	Cu	$3d^{10} 4s^1$
30	Zn	$3d^{10} 4s^2$

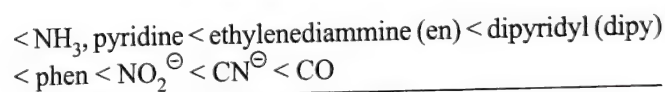
- For coordination number 4, the hybridisations possible are sp^3 and dsp^2 , having tetrahedral and square planar geometries respectively, while for coordination number 6, the hybridisations possible are d^2sp^3 and sp^3d^2 having octahedral geometry in both the cases.
- There are two types of ligands namely strong field and weak field. A strong field ligand is capable of forcing the electrons of the metal atom/ion to pair up (if required). A weak field ligand is incapable of making the electrons of the metal atom/ion to pair up.
- Some ligands have been arranged below from the weakest to the strongest. This arrangement is called spectro chemical series as shown below:



Weak field ligand



Border line field ligands



Strong field ligands

Note:

- This series has been determined experimentally and is not a postulate of VBT. However, we can use it to predict the structure, electronic configuration, magnetic properties etc. of a coordination complex.
- Ligands given in the borderline criteria act both as strong and weak field ligands. By knowing the value of magnetic moment, it may be suggested that whether they act as a strong and a weak ligand in a particular case.
- Generally NH_3 behaves as a strong field ligand and H_2O (or ligands nearby it in the series) as a weak field ligand. The compound $[Co(OX)_3]^{3-}$, is one of the few rare examples where oxalate (OX^{2-}) ligand acts as a strong field ligand.

Table 7.16 Some important types of hybridisation and their geometry

Coordination number	Types of hybridisation	Geometry of the complex	Examples
2	sp ($4s, 4p_x$)	Linear	$K[Ag(CN)_2]$, $[Ag(NH_3)_2]^+$ $[CuCl_2]^-$, $[Cu(NH_3)_2]^+$
3	sp^2 ($4s, 4p_x, 4p_y$)	Trigonal planar	$K[HgI_3]$
4	dsp^2 ($3d_{x^2-y^2}, 4s, 4p_x, 4p_y$)	Square planar	$[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$
4	$sp^2 d$ ($4s, 4p_x, 4p_y, 4d_{x^2-y^2}$)	Square planar	$[Cu(NH_3)_4]^{2+}$
4	sp^3 ($4s, 4p_x, 4p_y, 4p_z$)	Tetrahedral	$[NiCl_4]^{2-}$, $[Cu(CN)_4]^{3-}$, $[Ni(CO)_4]$
5	dsp^3 ($3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z$)	Trigonal bipyramidal	$[Fe(CO)_5]$, $[CuCl_5]^{3-}$
5	$sp^3 d$	Square pyramidal	$[SbF_5]^{2-}$
6	$d^2 sp^3$ ($3d_{x^2-y^2}, 3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z$)	Octahedral (Inner-orbital complex)	$[Ti(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$
6	$sp^3 d$ ($4s, 4p_x, 4p_y, 4p_z, 4d_{x^2-y^2}, 4d_{z^2}$)	Octahedral (Outer-orbital complex)	$[CoF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$

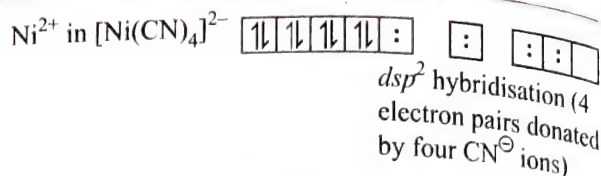
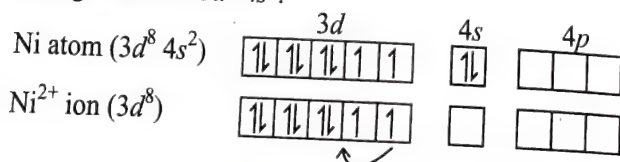
7.10.3 GEOMETRY OF FOUR-COORDINATED COMPLEXES

In these complexes, the coordination number of central atom/ion is four. Such complexes may have either square planar or tetrahedral geometry, depending on whether the central atom/ion is dsp^2 or sp^3 hybridised. According to Pauling's prediction, if the complex is paramagnetic it should have tetrahedral geometry, whereas for diamagnetic complex it should be square planar.

Some of the examples are as follows:

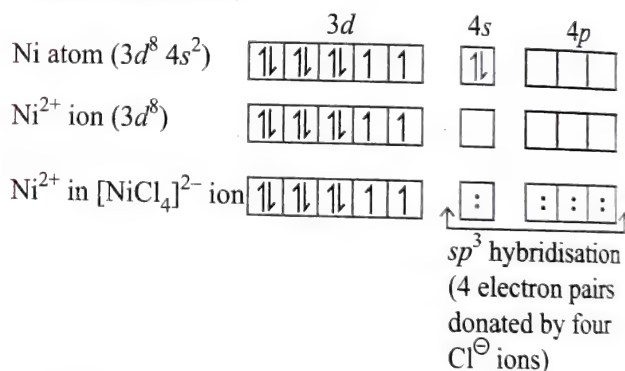
1. $[Ni(CN)_4]^{2-}$ ion: Oxidation state of Ni in $[Ni(CN)_4]^{2-}$ ion = +2

Ni atom in zero oxidation state/ground state has a configuration of $3d^8 4s^2$.



Since the complex is diamagnetic, the two unpaired electrons in $3d$, gets paired up making available one vacant $3d$ orbital. One $3d$, one $4s$ and two $4p$ orbitals hybridise to give four dsp^2 hybrid orbitals and these orbitals now participate in sigma bond formation with the ligands. Thus $[Ni(CN)_4]^{2-}$ ion has square planar geometry and such no unpaired electron is there, it is diamagnetic.

- CN^- being a strong ligand forces pairing of electron to 2-half filled $3d$ orbitals
 - Hybridisation: dsp^2
 - Geometry: square planar
 - Number of unpaired electrons = 0
 - Diamagnetic
 - $\mu_s = \text{zero BM}$
2. $[NiCl_4]^{2-}$ ion: This complex ion has Ni^{2+} ion whose valence shell configuration is $3d^8 4s^0$. Magnetic measurements reveal that the given ion is paramagnetic. This is possible only when this ion is formed by sp^3 hybridisation and has tetrahedral geometry.

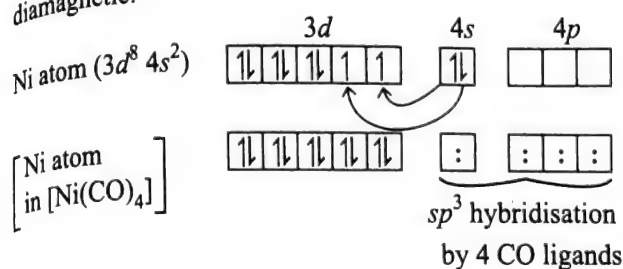


- Cl^- is a weak ligand, so no pairing of electrons occurs.
- Hybridisation: sp^3
- Geometry: Tetrahedral
- Number of unpaired electrons = 2
- Paramagnetic
- $\mu_s = \sqrt{2(2+2)} = 2.838 \text{ B.M.}$

Note:

- Thus the coordination entities $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ illustrate the useful rule originally called "the magnetic criteria of bond type". That is, the geometry of a coordinated entity can be predicted if its magnetic properties are known. In above case this theory allows prediction of geometry of a four coordinated d^8 complex. If the complex is diamagnetic then its shape will be "square planar" and if it is paramagnetic then its shape will be "tetrahedral".
- The above generalisation of VB theory is not accurate and is one of its drawbacks.

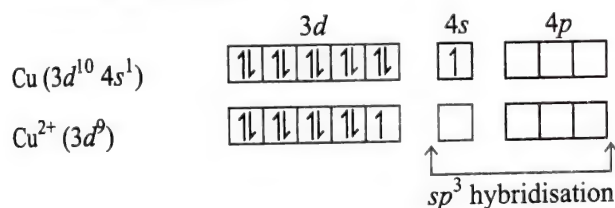
3. **[Ni(CO)₄]:** Oxidation state of Ni in [Ni(CO)₄] is zero. Magnetic measurements reveal that the complex is diamagnetic.



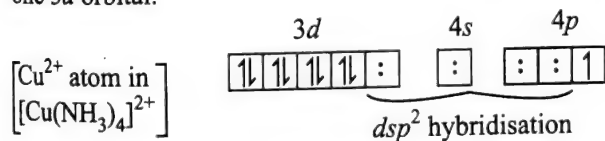
Ni in [Ni(CO)₄] undergoes sp^3 hybridisation and hence [Ni(CO)₄] has tetrahedral geometry. In this example, Pauling's prediction that if the complex is diamagnetic, it should have square planar geometry but it was found to have tetrahedral geometry.

- The CO ligand is a strong ligand, so pairing of e^- 's in 2-half-filled 3d orbitals occurs from 4s orbitals.
- Hybridisation: sp^3
- Geometry: Tetrahedral
- Diamagnetic
- $\mu_s = \text{zero BM}$

4. **[Cu(NH₃)₄]²⁺:** Coordination number of Cu²⁺ in [Cu(NH₃)₄]²⁺ is four. Hence according to VBT, its geometry can be square planar or tetrahedral. Magnetic measurements have predicted this complex to be square planar.

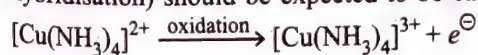


For [Cu(NH₃)₄]²⁺ to have square planar, Pauling predicted a promotion of an electron from 3d to 4p. Making available one 3d orbital.



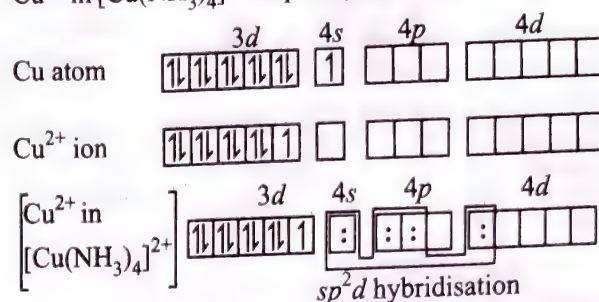
- Hybridisation: dsp^2
- Geometry: Square planar
- Number of unpaired electron = 1
- $\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.732 \text{ BM}$

If square planar geometry is correct, then the unpaired electron present in higher energy 4p orbital (dsp^2 hybridisation) should be expected to be easily lost, i.e.



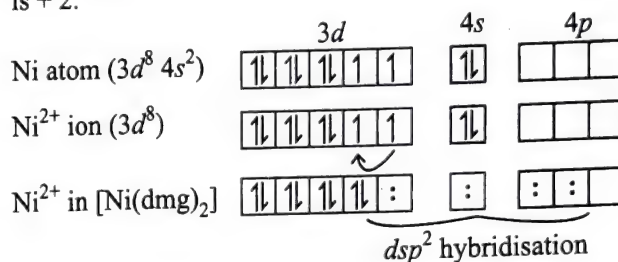
However, experiments have shown that [Cu(NH₃)₄]²⁺ does not undergo oxidation. This was explained by Huggin.

Huggin suggested that [Cu(NH₃)₄]²⁺ has square planar geometry, unpaired electron in Cu²⁺ resides in 3d-orbital and Cu²⁺ in [Cu(NH₃)₄]²⁺ is sp^2d hybridised as shown below:



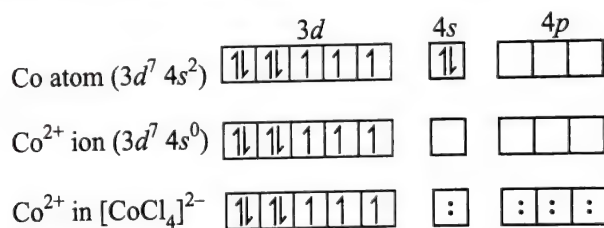
Complex ion is paramagnetic with one unpaired electron.

5. **[Ni(dmg)₂] molecule:** Oxidation state of Ni in [Ni(dmg)₂] is +2.



- The (dmg) is a strong ligand so pairing of one electron in 2-half-filled 3d orbitals occurs.
- Hybridisation: dsp^2
- Geometry: Square planar
- Number of unpaired electron = zero
- Diamagnetic
- $\mu_s = \text{zero BM}$

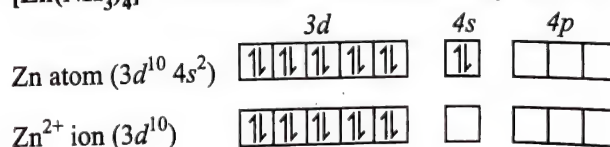
6. **[CoCl₄]²⁻:** Oxidation state of Co in [CoCl₄]²⁻ is +2.

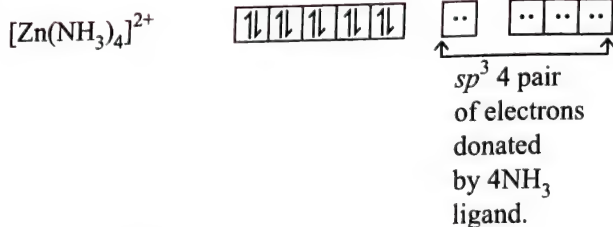


sp^3 hybridisation (four electron pairs donated by 4 Cl⁻ ions, forming tetrahedral geometry)

- Cl⁻ being weak ligand is unable to force the pairing of electrons.
- Hybridisation: sp^3
- Geometry: Tetrahedral
- Number of unpaired electrons = 3
- Paramagnetic
- $\mu_s = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ B.M.}$

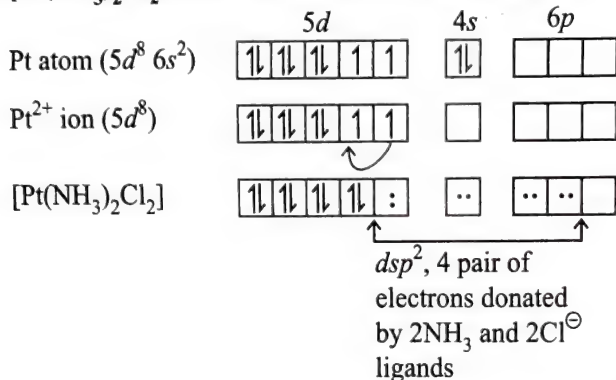
7. **[Zn(NH₃)₄]²⁺:** Oxidation state of Zn in complex = +2.





- Hybridisation: sp^3
- Geometry: Tetrahedral
- Number of unpaired electron = 0
- Diamagnetic
- μ_s = zero BM

8. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$: Oxidation state of Pt in the complex = + 2.



- NH_3 being a strong ligand forces pairing of electrons of 2 half-filled $5d$ -orbitals.
- Hybridisation: dsp^2
- Geometry: Square planar
- Number of unpaired electron = 0
- Diamagnetic
- μ_s = zero BM

ILLUSTRATION 7.40

The spin only magnetic moment value of $[\text{MnBr}_4]^{2-}$ ion is 5.9 BM. On the basis of VBT predict the hybridisation and geometry of $[\text{MnBr}_4]^{2-}$ ion.

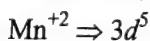
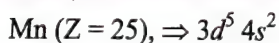
Sol. Oxidation state of Mn in the complex = +2. Since the coordination number of Mn^{+2} ion in the complex = 4.

Therefore it will be either tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation).

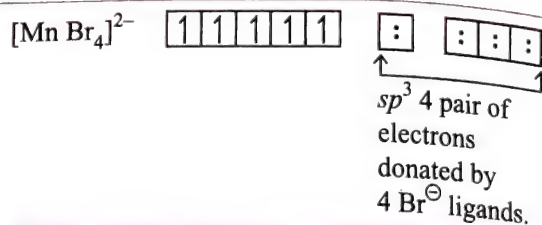
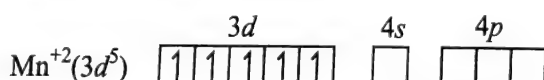
But the fact that the magnetic moment of the complex is 5.9 BM (given), which corresponds to n (number of unpaired electrons) = 5.

Due to the presence of 5 unpaired electrons in the $3d$ orbitals of Mn^{+2} , it should be tetrahedral in shape rather than square planar.

If the geometry of the complex ion is tetrahedral

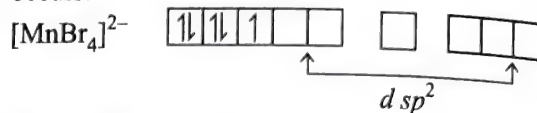


Since Br^- is a weak ligand so pairing of electrons in the five half-filled $3d$ orbitals will not occur.



If the geometry of the complex ion is square planar

If the pairing of electrons in the five half-filled $3d$ orbitals occurs.

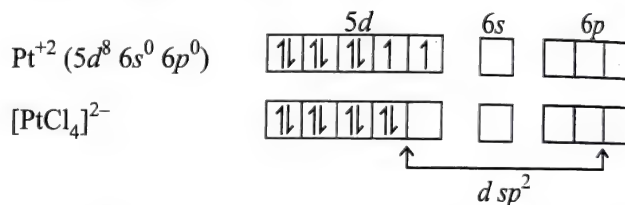
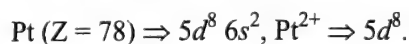


The number of unpaired electron in the complex should be equal to one. So μ_s should be equal to $\sqrt{3} = 3.83$ BM which is not given. Hence hybridisation is not dsp^2 but sp^3 .

ILLUSTRATION 7.41

Predict the number of unpaired electrons in square planar $[\text{PtCl}_4]^{2-}$ ion.

Sol. Oxidation state of Pt in $[\text{PtCl}_4]^{2-}$ ion is +2. Pt^{2+} is $5d^8$ ion. For square planar geometry dsp^2 hybridisation is required. For the availability of one d -orbital, pairing of electrons takes place in the remaining d -orbitals. Hence there should be no unpaired electrons in $[\text{PtCl}_4]^{2-}$ ion.



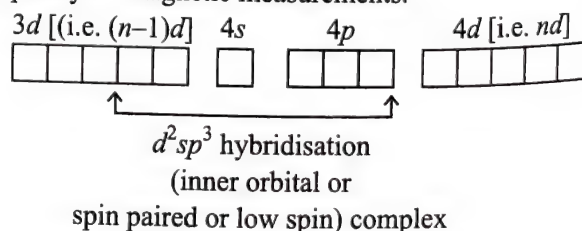
Since Cl^- being weak ligand, so pairing of $3d$ electrons should not occur, but for square planar complex (dsp^2 hybridisation, pairing of electrons in 2 half-filled $5d$ orbitals occurs.

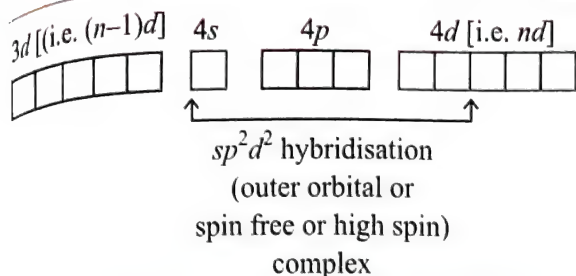
It is a limitation of VB theory.

7.10.4 GEOMETRY OF SIX-COORDINATED COMPLEXES

Valence bond theory explains the formation of 6-coordinate octahedral coordination entities by involving the use of $(n-1)d^2 ns np^3$ or $ns np^3 nd^2$ hybrid orbitals by the central atom/ion in forming bonds with the ligands i.e. octahedral geometry arises due to d^2sp^3 or sp^3d^2 hybridization of the central atom ion. Octahedral complexes in which the central atom is d^2sp^3 hybridised are called **inner-orbital octahedral complex**, while the octahedral complexes in which the central atom is sp^3d^2 hybridised are called **outer orbital octahedral complexes** as shown below.

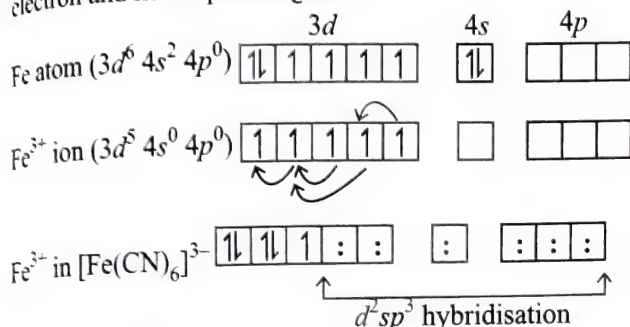
This distinction between inner and outer orbital complex is based purely on magnetic measurements.





10.5 SOME EXAMPLES OF INNER ORBITAL COMPLEXES

1. $[\text{Fe}(\text{CN})_6]^{3-}$ (hexacyanoferrate(II) ion): Magnetic studies of $[\text{Fe}(\text{CN})_6]^{3-}$ ion has shown that this ion has one unpaired electron and hence paramagnetic.



i. CN^- being a strong ligand force pairing of 5-half filled $3d$ orbitals

ii. Hybridisation: $d^2 sp^3$

iii. Geometry: Octahedral

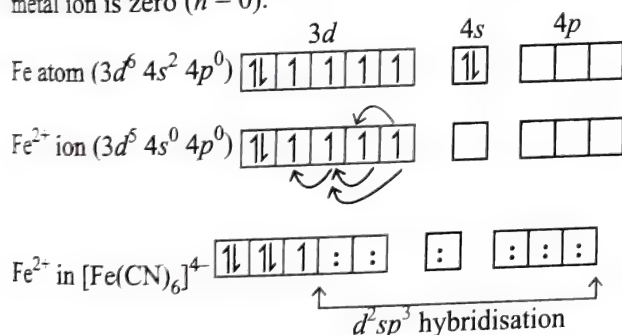
iv. Inner orbital or low spin or spin paired complex.

v. Number of unpaired electron = 1

vi. Paramagnetic

vii. $\mu_s = \sqrt{3} = 1.732$ BM

2. $[\text{Fe}(\text{CN})_6]^{4-}$ ion (hexacyanoferrate(II) ion): Magnetic studies of $[\text{Fe}(\text{CN})_6]^{4-}$ ion have shown that this complex ion is diamagnetic, i.e. number of unpaired electron on central metal ion is zero ($n = 0$).



It is due to $d^2 sp^3$ hybridisation that $[\text{Fe}(\text{CN})_6]^{4-}$ is an inner orbital octahedral complex. The electron pair donated by CN^- ion (ligand) is accommodated in each of the six $d^2 sp^3$ hybrid orbital as shown above.

i. CN^- being a strong ligand force pairing of 4 half-filled $3d$ orbitals

ii. Hybridisation: $d^2 sp^3$

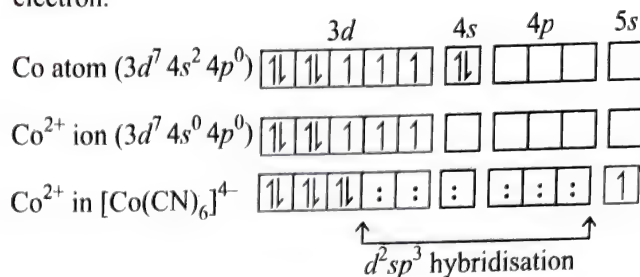
iii. Geometry: Octahedral

iv. Inner orbital or low spin or spin paired complex.

v. Number of unpaired electron = 0

vi. Diamagnetic $\mu_s = \text{zero BM}$

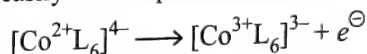
3. $[\text{Co}(\text{CN})_6]^{4-}$ (hexacyanocobalt(II) ion): $[\text{Co}(\text{CN})_6]^{4-}$ ion is paramagnetic corresponding to the presence of one unpaired electron.



The valence shell electronic configuration of Co^{2+} ion in free state is $(3d^7 4s^0 4p^0 5s^0)$, in the complex ion, $[\text{Co}(\text{CN})_6]^{2-}$ electronic configuration is $3d^6 4s^0 4p^0 5s^1$.

Pauling has suggested that in order to have only one unpaired electron, one electron is forced to pair up in $3d$ -orbital, and remaining one unpaired is promoted to $4s$.

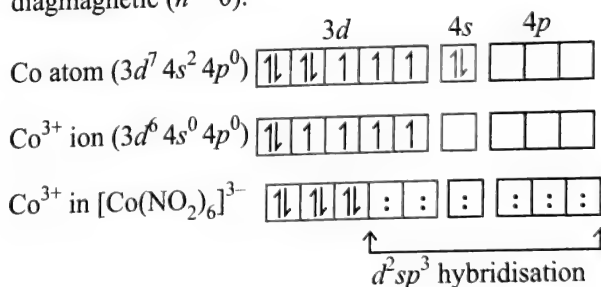
The presence of unpaired electron in $5s$ is supported by the fact that since $5s$ orbital is of high energy, the one unpaired electron residing in it should be unstable and hence should be easily lost. Experimentally it has been found to be true.



When $[\text{CoL}_6]^{4-}$ is acted upon by air or H_2O_2 , the complex easily gets oxidised to $[\text{CoL}_6]^{3-}$, thereby losing the unpaired electron present in $5s$ orbital.

Thus we conclude that Co^{2+} inner orbital octahedral complexes are unstable (or labile) and hence gets easily oxidised to Co^{3+} complexes by air or H_2O_2 . Consequently, such complexes should be prepared in an inert atmosphere.

4. $[\text{Co}(\text{NO}_2)_6]^{3-}$ (hexanitrito-N-cobaltate(III) ion): Magnetic studies reveal that the given complex is diamagnetic ($n = 0$).



Since the complex is diamagnetic, all the electrons in $3d$ -orbital gets paired up.

i. NO_2^- being a strong ligand forces pairing of 4 half-filled $3d$ orbitals.

ii. Hybridisation: $d^2 sp^3$

iii. Geometry: Octahedral

iv. Inner orbital or spin paired or low spin complex.

v. Number of unpaired electron = 0

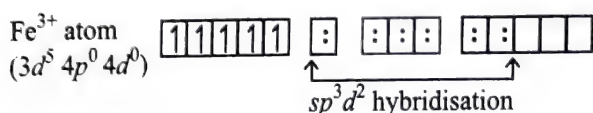
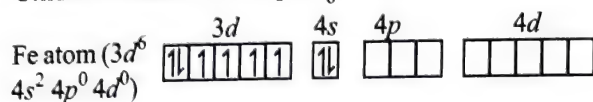
vi. Diamagnetic

vii. $\mu_s = 0$

Note: Oxalate, generally behaves as weak field ligand but with Co(cobalt), it behaves as a strong field ligand like NH_3 e.g., in the compound $[\text{Co}(\text{OX})_3]^{3-}$.

7.10.5.1 Some Examples of Outer Orbital Octahedral Complexes

1. **$[\text{FeF}_6]^{3-}$ ion (hexafluoridoferrate(III) ion):** In $[\text{FeF}_6]^{3-}$, CN of Fe is six, hence $[\text{FeF}_6]^{3-}$ ion has octahedral geometry. Oxidation state of Fe in $[\text{FeF}_6]^{3-}$ is +3.

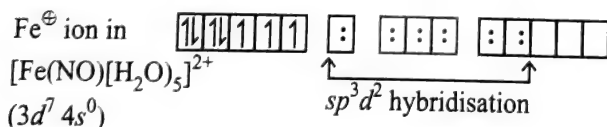
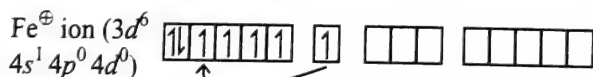
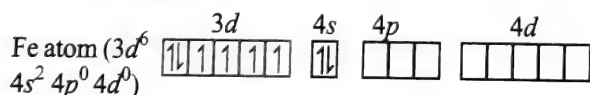


There are five unpaired electrons and hence $n = 5$. Magnetic properties also reveal that $[\text{FeF}_6]^{3-}$ ion is paramagnetic. The two d -orbitals used in $sp^3 d^2$ hybridisation are $4d_{z^2}$ and $4d_{x^2-y^2}$ and not $3d_{z^2}$ and $3d_{x^2-y^2}$.

- F^- being a weak ligand is unable to pair 5 half-filled $3d$ electrons.
- Hybridisation: $sp^3 d^2$
- Geometry: Octahedral
- Outer orbital or spin free or high spin complex.
- Number of unpaired electrons = 5
- Paramagnetic
- $\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}$

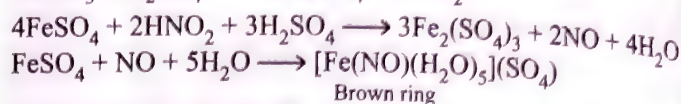
2. **$[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$ ion (pentaquanitrosoniumiron(I) ion):**

$[\text{Fe}^\oplus(\text{NO})^\oplus(\text{H}_2\text{O})_5]^{2+}$ ion CN of Fe is six, hence it has octahedral geometry. Oxidation state of Fe in $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$ ion is +1.

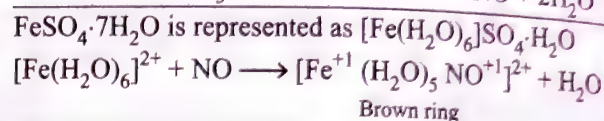
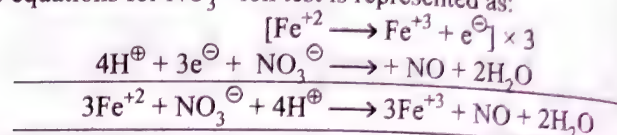


- NO^\oplus is a strong ligand so forces the pairing of only one unpaired $3s$ electron to one half-filled orbital of $3d$.
- Hybridisation: $sp^3 d^2$
- Geometry: Octahedral
- Outer orbital complex.
- Number of unpaired electrons = 3
- Paramagnetic
- $\mu_s = \sqrt{15} = 3.83 \text{ BM}$

Note: $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$ ion is formed in the brown ring test for the confirmation of nitrate ion in the salt analysis. To the nitrate solution, equal volume of freshly prepared saturated solution of FeSO_4 is added. To this solution, conc. H_2SO_4 is added slowly from the side of the test tube so that acid forms a layer beneath the mixture. A brown ring is formed at the function of the two liquids, due to formation $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5](\text{SO}_4)$.

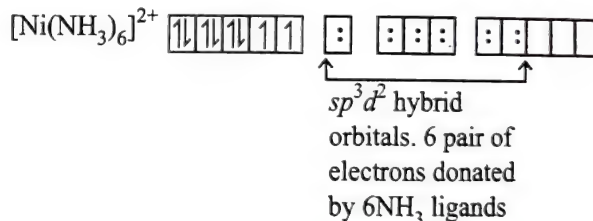
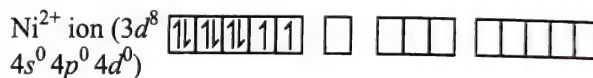
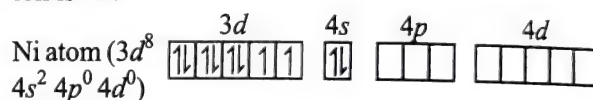


Ionic equations for NO_3^- ion test is represented as:



3. **$[\text{Ni}(\text{NH}_3)_6]^{2+}$ ion (hexaamminenickelate(II) ion):**

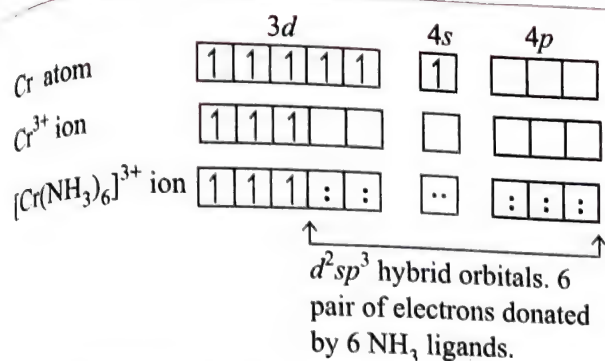
$[\text{Ni}(\text{NH}_3)_6]^{2+}$ ion CN of Ni is six, hence $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ion has octahedral geometry. Oxidation state of Ni in $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ion is +2.



Note: With most of the central metal/ion, NH_3 behaves as a strong ligand but with some metal/ion e.g. Ni^{2+} ion, it behaves as a weak ligand.

The above generalisation of V.B. theory is not accurate and is one of its drawbacks.

- In the above complex NH_3 being weak ligand is not able to force pairing of electrons.
 - Hybridisation: $sp^3 d^2$
 - Geometry: Octahedral
 - Outer orbital or spin free or high spin complex.
 - Number of unpaired electrons = 2
 - Paramagnetic
 - $\mu_s = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ BM}$
4. **$[\text{Cr}(\text{NH}_3)_6]^{3+}$ (Hexaminechromium(III) ion):**
Oxidation state of Cr = +3, coordination number (CN) of Cr^{3+} ion = 6.
Valence electronic configuration of:
Cr atom $\Rightarrow 3d^5 4s^1$, Cr^{3+} ion $\Rightarrow 3d^3$



i. Hybridisation: $d^2 sp^3$ ii. Geometry: Octahedral

iii. Inner orbital or spin paired or low spin complex.

iv. Number of unpaired electron = 3

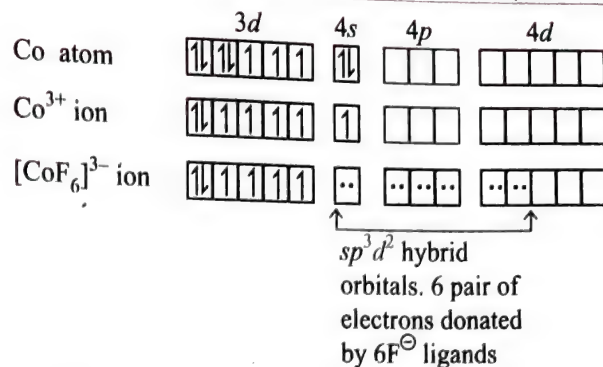
v. Paramagnetic

vi. $\mu_s = \sqrt{3(3+2)} = \sqrt{15} = 3.287 \text{ BM}$

5. [CoF₆]³⁻ (Hexafluoridocobaltate(III) ion): Oxidation state of Co = +3, coordination number (CN) of Co³⁺ ion = 6.

Valence electronic configuration of:

Co atom $\Rightarrow 3d^7 4s^2$, Co³⁺ ion = $3d^6$.



i. F⁻ being a weak ligand is not able to force pairing of electrons.

ii. Hybridisation: $sp^3 d^2$

iii. Geometry: Octahedral

iv. Outer orbital or spin free or high spin complex.

v. Number of unpaired electrons = 4

vi. Paramagnetic

vii. $\mu_s = \sqrt{4(4+2)} = \sqrt{24} = 4.90 \text{ BM}$

Table 7.17 Geometry (shape) hybridisation and magnetic nature of some of the complexes (application of valence bond theory)

Atom/ion complex	Configuration	Oxidation state of metal	Hybridization	Geometry (Shape)	No. of unpaired electrons	Magnetic nature
1	2	3	4	5	6	7
A						
Sc ³⁺ (d^0)	$3d^0 4s^0 4p^0$	+3	—	—	0	Diamagnetic
[ScF ₆] ³⁻	$3d^0 4s^0 4p^0$ with 6 pairs of electrons donated by 6 F ⁻ ligands.	+3	$d^2 sp^3$ (inner)	Octahedral	0	Diamagnetic
B						
Ti ³⁺ (d^1)	$3d^1 4s^0 4p^0$	+3	—	—	—	Paramagnetic
[TiF ₆] ³⁻	$3d^1 4s^0 4p^0$ with 6 pairs of electrons donated by 6 F ⁻ ligands.	+3	$d^2 sp^3$ (inner)	Octahedral	1	Paramagnetic
[Ti(H ₂ O) ₆] ³⁺	$3d^1 4s^0 4p^0$ with 6 pairs of electrons donated by 6 H ₂ O ligands.	+3	$d^2 sp^3$ (inner)	Octahedral	1	Paramagnetic
Ti ⁴⁺ (d^0)	$3d^0 4s^0 4p^0$	+4	—	—	0	Diamagnetic
[TiX ₆] ²⁻	$3d^0 4s^0 4p^0$ with 6 pairs of electrons donated by 6 X ⁻ ligands.	+4	$d^2 sp^3$ (inner)	Octahedral	0	Diamagnetic

C						
$V^{3+} (d^2)$		+3	—	—	2	Paramagnetic
$[V(H_2O)_6]^{3+}$		+3	d^2sp^3 (inner)	Octahedral	2	Paramagnetic
D						
$Cr^{3+} (d^3)$		+3	—	—	3	Paramagnetic
$[Cr(H_2O)_6]^{3+}$		+3	d^2sp^3 (inner)	Octahedral	3	Paramagnetic
$[Cr(NH_3)_6]^{3+}$		+3	d^2sp^3 (inner)	Octahedral	3	Paramagnetic
$[Cr(CN)_6]^{3-}$		+3	d^2sp^3 (inner)	Octahedral	3	Paramagnetic
$[CrF_6]^{3-}$		+3	d^2sp^3 (inner)	Octahedral	3	Paramagnetic
$[Cr(NH_3)_4Cl_2]^{\oplus}$		+3	d^2sp^3 (inner)	Octahedral	3	Paramagnetic
$Cr^0 (d^5s^1)$		0	—	—	5	Paramagnetic
$[Cr(CO)_6]$		0	d^2sp^3 (inner)	Octahedral	0	Diamagnetic
$Cr^{2+} (d^4)$		+2	—	—	4	Paramagnetic
$[Cr(CN)_6]^{4-}$		+2	d^2sp^3 (inner)	Octahedral	0	Diamagnetic
$[Cr(H_2O)_6]^{2+}$		+2	sp^3d^2 (outer)	Octahedral	4	Paramagnetic
$[Cr(NH_3)_6]^{2+}$		+2	sp^3d^2 (outer)	Octahedral	4	Paramagnetic
E						
$Mn^{+1} (3d^54s^1)$		+1	—	—	6	Paramagnetic
$[Mn(CN)_6]^{5-}$		+1	d^2sp^3 (inner)	Octahedral	0	Diamagnetic

$Mn^{2+} (3d^5)$		+2	—	—	5	Paramagnetic
$[Mn(CN)_6]^{4-}$		+2	d^2sp^3 (inner)	Octahedral	1	Paramagnetic
$[MnCl_4]^{2-}$		+2	sp^3	Tetrahedral	5	Paramagnetic
$[MnBr_4]^{2-}$		+2	sp^3	Tetrahedral	5	Paramagnetic
$[Mn(H_2O)_6]^{2+}$		+2	sp^3d^2 (outer)	Octahedral	5	Paramagnetic
$Mn^{3+} (3d^4)$		+3	—	—	4	Paramagnetic
$[MnF_6]^{3-}$		+3	sp^3d^2 (outer)	Octahedral	4	Paramagnetic
$[Mn(acac)_3]^0$		+3	sp^3d^2 (outer)	Octahedral	4	Paramagnetic
$[Mn(CN)_6]^{3-}$		+3	sp^3d^2 (inner)	Octahedral	0	Diamagnetic
F						
$Fe (3d^6 4s^2)$		0	—	—	4	Paramagnetic
$Fe(CO)_5$		0	dsp^3 (inner)	Trigonal bipyramidal	0	Diamagnetic
$Fe^{\oplus} (3d^6 4s^1)$		+1	—	—	5	Paramagnetic
$[Fe(H_2O)_5(NO)]^{2+}$		+1	sp^3d^2 (outer)	Octahedral	3	Paramagnetic
$Fe^{2+} (3d^6)$		+2	—	—	4	Paramagnetic
$[Fe(NH_3)_6]^{2+}$		+2	sp^3d^2 (outer)	Octahedral	4	Paramagnetic
$[Fe(H_2O)_6]^{2+}$		+2	sp^3d^2 (outer)	Octahedral	4	Paramagnetic
$[Fe(CN)_6]^{4-}$		+2	d^2sp^3 (inner)	Octahedral	0	Diamagnetic
$[FeCl_4]^{2-}$		+2	sp^3	Tetrahedral	4	Paramagnetic

$\text{Fe}^{3+} (3d^5)$		+3	—	—	5	Paramagnetic
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$		+3	sp^3d^2 (outer)	Octahedral	5	Paramagnetic
$[\text{FeF}_6]^{3-}$		+3	sp^3d^2 (outer)	Octahedral	5	Paramagnetic
$[\text{Fe}(\text{CN})_6]^{3-}$		+3	d^2sp^3 (inner)	Octahedral	1	Paramagnetic
$[\text{FeCl}_4]^-$		+3	sp^3	Tetrahedral	5	Paramagnetic

G

$\text{Co}^{2+} (d^7)$		+2	—	—	3	Paramagnetic
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$		+2	sp^3d^2 (outer)	Octahedral	3	Paramagnetic
$[\text{CoCl}_4]^{2-}$		+2	sp^3	Tetrahedral	3	Paramagnetic
$[\text{Co}(\text{CN})_6]^{4-}$		+2	d^2sp^3 (inner)	Octahedral	1 e^- (in 5s orbital)	Paramagnetic
$[\text{Co}(\text{NO}_2)_6]^{4-}$		+2	d^2sp^3 (inner)	Octahedral	1 e^- (in 5s orbital)	Paramagnetic
$\text{Co}^{3+} (d^6)$		+3	—	—	4	Paramagnetic
$[\text{Co}(\text{NH}_3)_6]^{3+}$		+3	d^2sp^3 (inner)	Octahedral	0	Diamagnetic

Note: NH_3 acts as weak ligand for Co^{2+} and strong ligand for Co^{3+} ion.

$[\text{Co}(\text{NO}_2)_6]^{3-}$		+3	d^2sp^3 (inner)	Octahedral	0	Diamagnetic
$[\text{Co}(\text{CN})_6]^{3-}$		+3	d^2sp^3 (inner)	Octahedral	0	Diamagnetic
$[\text{CoF}_6]^{3-}$		+3	d^2sp^3 (outer)	Octahedral	4	Paramagnetic

H

$\text{Ni}(3d^8 4s^2)$		0	—	—	2	Paramagnetic
$\text{Ni}(\text{CO})_4$		0	sp^3	Tetrahedral	0	Diamagnetic

$Ni^{2+}(d^8)$		+2	—	—	2	Paramagnetic
$Ni(NH_3)_6^{2+}$		+2	sp^3d^2 (outer)	Octahedral	2	Diamagnetic
$NiCl_4^{2-}$		+2	sp^3	Tetrahedral	2	Paramagnetic
$Ni(CN)_4^{2-}$		+2	dsp^2	Square planar	0	Diamagnetic
$Ni(dmg)_2$		+2	dsp^2	Square planar	0	Diamagnetic
$Ni(big H)_2^{2+}$		+2	dsp^2	Square planar	0	Diamagnetic
$Ni(NH_3)_4^{2+}$		+2	sp^3	Tetrahedral	2	Diamagnetic
I						
$Zn^{2+}(d^0)$		+2	—	—	1	Paramagnetic
$ZnCl_4^{2-}$		+2	sp^3	Tetrahedral	1	Paramagnetic
$[Zn(NH_3)_4]^{2+}$		+2	dsp^2	Square planar	1	Paramagnetic
Note: $[Cu(NH_3)_4]^{2+}$ is expected to be sp^3 hybridised but $[Cu(NH_3)_4]^{2+}$ is square planar (experimentally determined), and hence dsp^2 hybridised. But according to Huggin, it is sp^2d hybridisation (Refer to Section 7.10.3, Point 4).						
$[Cu(CN)_4]^{2-}$		+2	sp^3	Tetrahedral	1	Paramagnetic
$Zn^{2+}(d^0)$		+1	—	—	0	Diamagnetic
$[Zn(CN)_4]^{3-}$		+1	sp^3	Tetrahedral	0	Diamagnetic
J						
$Zn^{2+}(d^0)$		0	—	—	0	Diamagnetic
$[Zn(NH_3)_6]^{2+}$ in crystal only		0	sp^3d^2 (outer)	Octahedral	0	Diamagnetic

7.10.6 LIMITATIONS OF VBT

While the valence bond theory to a large extent explains the formation, structure and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:

1. VBT fails to explain the finer details of magnetic

properties including the magnitude of orbital contribution to the magnetic moments, e.g. both tetrahedral (sp^3 hybridisation) and outer orbital octahedral (sp^3d^2 hybridisation) complexes of $Co(+2)$ (d^7 system) have three unpaired electrons and are therefore expected to have $\mu_s = 3.87$ BM. The tetrahedral complexes have generally

μ_s = value in the range of 4.4–4.8 BM, while the octahedral complexes have μ_s in the range of 4.7–5.2 BM VBT cannot explain the increase in value of μ_s .

- It does not explain the variation of magnetic properties of complex with temperature.
- The magnetic moment values of complexes of certain ions (e.g. Co^{2+} , Ni^{2+} etc.) are much higher than those expected by spin only formula. VBT cannot explain the enhanced values of magnetic moment.
- VBT cannot interpret the spectra (color) of the complexes.
- VBT cannot explain as to why Cu^{2+} forms only distorted octahedral complexes even when all the six ligands are identical.
- It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
- It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of the coordination compounds.
- It does not explain why in some complexes, metal ion forms inner orbital complex (d^2sp^3 , low spin complexes) whereas others form outer orbital complexes (sp^3d^2 , high spin complexes).
- It does not distinguish between strong and weak ligands.

ILLUSTRATION 7.42

Magnetic moment value of $[\text{Mn}(\text{CN})_6]^{3-}$ ion in 2.8 BM. Predict the type of hybridisation and geometry of the ion.

Sol. $\mu_s = 2.8$ BM corresponds to $n = 2$.

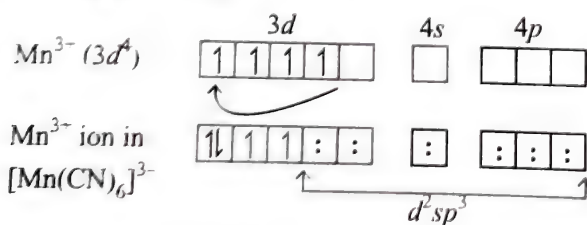
Note: Short method to calculate 'n' (number of unpaired electrons if μ_s is given)

Take $2.8 \text{ BM} \approx 3 \text{ B.M.}$, then take its square which is 9 and then take its underroot $\sqrt{9}$ which is nearly equal to $\sqrt{8}$ BM when $\mu_s = \sqrt{8}$ BM, then $n = 2$.

Thus Mn in $[\text{Mn}(\text{CN})_6]^{3-}$ has two unpaired electrons ($n = 2$).

Oxidation state of Mn in $[\text{Mn}(\text{CN})_6]^{3-}$ is +3, Mn ($Z = 25$)

$\Rightarrow 3d^5 4s^2$ and $\text{Mn}^{+3} = 3d^4$



- CN^- being a strong ligand, forces only one pairing of 4 half-filled $3d$ orbitals.

Remember:

- In d^3 type electronic configuration, no pairing occurs whether the ligand is strong or weak.
- In d^4 type electronic configuration, only one pairing occurs if the ligand is strong.
- Thus the hybridisation is d^2sp^3 with octahedral geometry.
- Inner orbital complex.

ILLUSTRATION 7.43

Magnetic moment value of $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$ ion in 3.89 B.M. Find out the oxidation state of iron and type of hybridisation.

Sol. $\mu_s = 3.89$ BM corresponds to $n = 3$.

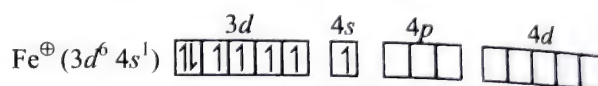
Take $3.89 \approx 4 \Rightarrow \sqrt{16} \approx \sqrt{15}$ B.M.

The value $\sqrt{15}$ BM corresponds to $n = 3$.

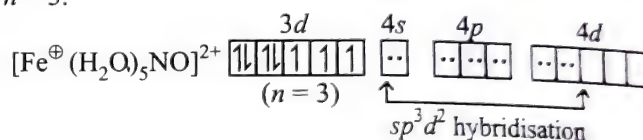
The oxidation state of Fe in the complex.

$[\text{Fe}^{+1}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ is +1 and CN of $\text{Fe}^{\oplus} = 6$

Fe ($Z = 26$) $\Rightarrow 3d^6 4s^2$, $\text{Fe}^{\oplus} = 3d^6 4s^1$



Since NO^{\oplus} is a strong ligand and H_2O is a weak ligand so only one pairing of $3d$ and $4s$ electrons occurs which also corresponds to $n = 3$.



- Oxidation state of Fe = +1
- Hybridisation = sp^3d^2
- Geometry = octahedral
- Outer orbital complex.

ILLUSTRATION 7.44

In what respects do inner orbital octahedral complexes differ from outer orbital octahedral complexes.

Sol. The differences between inner orbital and outer orbital octahedral complexes have been given in the following table:

Inner orbital octahedral complexes	Outer orbital octahedral complexes
i. The octahedral hybridisation used in the structure of these complexes involves the use of two ($n-1$) d , one ns and three np orbitals. In case of $3d$ -block elements this hybridisation is represented as $(3d)^2 (4s) (4p)^3$ or simply d^2sp^3	i. The octahedral hybridisation used in the structure of these complexes involves the use of one ns , three np and two nd orbitals. In case of $3d$ -block elements this hybridisation is represented as $(4s) (4p)^3 (4d)^2$ or simply as sp^3d^2
ii. These complexes are given by strong ligands	ii. These complexes are given by weak ligands

iii.	In these complexes strong ligands force the metal d-electrons to pair up and hence these complexes generally have paired electrons (diamagnetic) or lesser number of unpaired electrons (weakly paramagnetic)	iii.	In these complexes weak ligands are not able to pair up d-electrons and hence the valence shell configuration of the metal in the free state and in the complex remains the same. Thus these complexes generally have larger number of unpaired electrons (strongly paramagnetic)
iv.	These complexes are also called low spin complexes	iv.	These complexes are also called high spin complexes

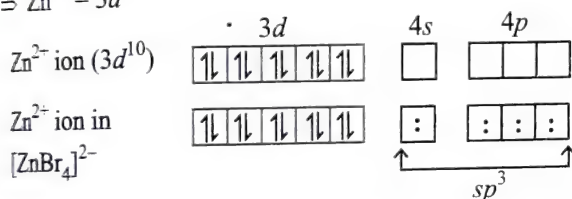
ILLUSTRATION 7.45

In $[\text{ZnBr}_4]^{2-}$ electron pairs in sp^3 hybrid orbitals of the zinc atom form bonds to the bromine atoms. Determine the number of unpaired electrons in the complex.

Sol. $[\text{ZnBr}_4]^{2-}$ oxidation state of Zn is +2.

Electronic configuration of Zn ($Z = 30$) $\Rightarrow 3d^{10}4s^2$

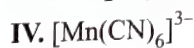
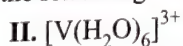
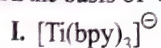
$\Rightarrow \text{Zn}^{2+} = 3d^{10}$



Since the d-orbitals are completely filled, there are no unpaired electrons.

CONCEPT APPLICATION EXERCISE 7.2

1. On the basis of VBT, answer the following complex ions:

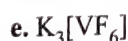
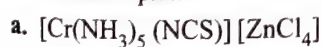


a. Type of hybridisation involved.

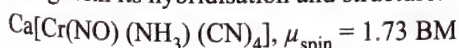
b. Type of inner or outer orbital octahedral complex.

c. Magnetic behaviour and μ_{spin} value.

2. Identify the complexes which are coloured and which are colourless. Explain.



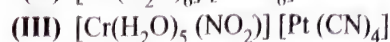
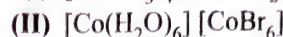
3. Write the IUPAC nomenclature of the given complex along with its hybridisation and structure.



4. On the basis of CFT, explain the following complexes of Co^{3+} like $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(\text{NO}_2)_6]^{3-}$

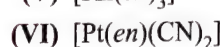
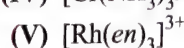
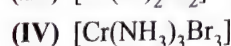
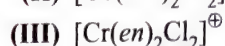
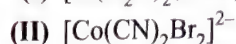
are diamagnetic while $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ are paramagnetic.

5. Consider the following complex compounds.



If a, b, c are more possible coordination isomers of given complex compounds respectively then calculate the value of $a + b + c$.

6. Consider the following complex compounds.



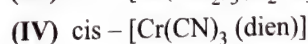
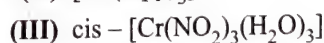
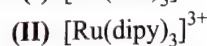
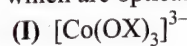
Calculate the sum total of geometrical isomers in all above compounds.

7. Total number of geometrical isomers of

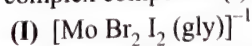
$[\text{PtBrClI}(\text{CN})(\text{H}_2\text{O})(\text{NH}_3)]^{2+}$ complex ion, is x and total number of geometrical isomers of the above compound when all the halide ions are in cis position is y then the value of $(x + y)$ is

8. For the complex compound $[\text{Cu}(\text{H}_2\text{O})_4][\text{PtBr}_4]$ if x is the number of more coordination isomers and for the compound $[\text{Cr}(\text{gly})(\text{en})_2]^{2+}$ if y is the number of stereoisomers, then $(x + y)$ is

9. Total number of complex compound among the following which are optically active?

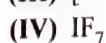
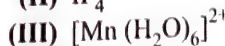
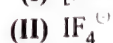
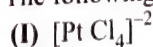


10. Total number of possible optically active isomers in complex compound (I) and (II) are:



11. Find out the total number of optically active isomers for complex compound having molecular formula $\text{Pt}x(\text{en})\text{Br}_4$, where $(x = 1, 2, 3)$

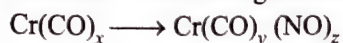
12. The following compounds are given:



If a is the total number of axial d-orbitals having zero nodal plane, b and c are total number of non-axial and axial d-orbitals respectively, each one having two nodal planes used in hybridisation of centrals of compounds I to IV.

Calculate the value of $a + b + c$.

13. Consider the following transformation



If both reactant and product follow EAN rule, then calculate the value of $x - (y + z)$.

14. Consider the following ligands:

- | | |
|-------------------------|--------------------------------------|
| (1) acac | (2) Phen |
| (3) DMG | (4) O_2^- |
| (5) NO_2^- | (6) NH_2^\ominus |
| (7) OH^\ominus | (8) Gly |
| (9) CO_3^{2-} | (10) en |
| (11) SO_4^{2-} | (12) $\text{CH}_3\text{COO}^\ominus$ |

If a = Total number of flexidentate ligands

b = Total number of ligands which acts as bridging as well as monodentate only

c = Total number of unsymmetrical bidentate ligands

d = Total number of bidentate ligands only.

Then calculate the value of $(a + b + c - d)$

15. 100 mL of 0.2 M solution of $\text{CrBr}_3 \cdot x\text{NH}_3$ was treated with excess of AgNO_3 solution and 0.04 moles of AgBr is precipitated. The value of $\frac{x}{2}$ is

16. Find out the number of compound(s) in which at least half of Br^\ominus ions are ionizable.

- | | |
|------------------------------------------|-------------------------------------------|
| (I) $\text{CoBr}_3 \cdot 6\text{NH}_3$ | (II) $\text{CoBr}_3 \cdot 5\text{NH}_3$ |
| (III) $\text{CoBr}_3 \cdot 4\text{NH}_3$ | (IV) $\text{CoBr}_3 \cdot 3\text{NH}_3$ |
| (V) $\text{PtBr}_4 \cdot 6\text{NH}_3$ | (VI) $\text{PtBr}_4 \cdot 5\text{NH}_3$ |
| (VII) $\text{PtBr}_4 \cdot 4\text{NH}_3$ | (VIII) $\text{PtBr}_4 \cdot 3\text{NH}_3$ |
| (IX) $\text{PtBr}_4 \cdot 2\text{NH}_3$ | |

17. Maximum number of N-atom that can lie in molecular plane of the complex $[\text{M}(\text{trien})]^{2+}$.

18. Find out the total number of ionic species/compounds in which central atom uses d^2 orbitals in its hybridisation.

- | | |
|----------------------------------------------|-------------------------------|
| (I) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ | (II) MnO_4^\ominus |
| (III) $[\text{PtI}_2(\text{NH}_3)_2]$ | (IV) $\text{Fe}(\text{CO})_5$ |
| (V) $[\text{Ni}(\text{CNS})_4]^{2-}$ | (VI) $[\text{CrBr}_5]^{3-}$ |
| (VII) $\text{Xe}^\ominus\text{F}_5$ | (VIII) ClF_5 |
| (IX) $\text{Ni}(\text{CO})_4$ | |

19. Find out the total number of diamagnetic inner orbital complexes.

- | | |
|-------------------------------------------------------------|----------------------------------------------------|
| (I) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ | (II) $\text{Ca}[\text{Fe}(\text{CNS})_5\text{NO}]$ |
| (III) $[\text{Cu}(\text{NH}_3)_4]\text{S}_2\text{O}_3$ | (IV) $\text{Ca}_2[\text{Co}(\text{CNS})_6]$ |
| (V) $\text{Na}_3[\text{Co}(\text{OX})_3]$ | (VI) $\text{Ca}[\text{NiBr}_4]$ |
| (VII) $\text{Na}_3[\text{Fe}(\text{CNS})_6]$ | (VIII) $\text{Na}_3[\text{Cr}(\text{SNC})_6]$ |
| (IX) $\text{Ca}[\text{PtBr}_4]$ | |

20. If x = maximum number of C-atoms that lie in a plane.

y = Number of C-atoms which are sp^3 hybridised.

z = Number of C-atoms which are sp^2 hybridised.

Then, find out the value of $(x + y - 3)$ for the complex $[\text{Ni}(\text{dmg})_2]$

21. If x = Total number of electron(s) in axial d -orbitals of inner shell of central atom ion in the complex $[\text{Co}(\text{CN})_6]^{3-}$

y = Total number of electrons in non-axial d -orbitals of inner shell of central metal ion in the complex $\text{Co}(\text{dmg})_2$. Then calculate the value of $(x + y)$.

22. Consider the following transformation.



Find the value of $(x + y - n)$.

7.11 CRYSTAL FIELD THEORY (CFT)

Crystal field theory is now much more widely accepted than the valence bond theory (VBT). This theory was proposed by Bathe and Van Vleck in 1930 and popularised by Orgel in 1952. CFT is an electrostatic model which considers the metal ligand bond ($\text{M} \leftarrow \text{L}$) to be ionic arising purely from electrostatic interaction between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules which have a lone pair of electrons. If the ligand is a neutral molecule such as NH_3 and H_2O , the negative end of the dipole in the molecule is directed towards the metal ion. The electrons of the central metal are under repulsive force from those of the ligands. Thus the outermost electrons in the d -orbitals of central transition metal atom/ion occupy those d -orbitals which are far away from the direction of approach of ligands.

In CFT, the following assumptions are made

1. Ligands are treated as point charges.
2. There is no interaction between metal orbitals and ligand orbitals.
3. The arrangement of the ligands around the central metal ion is such that the repulsion between these negative points is minimum.
4. **Splitting of d -orbital energies:** The five d -orbitals in an isolated gaseous metal atom/ion, have same energy i.e. they are degenerate (as shown in Fig. 7.28). This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion, but all of them will be raised in energy as a result of repulsion between the negative field and the electrons in the orbitals.

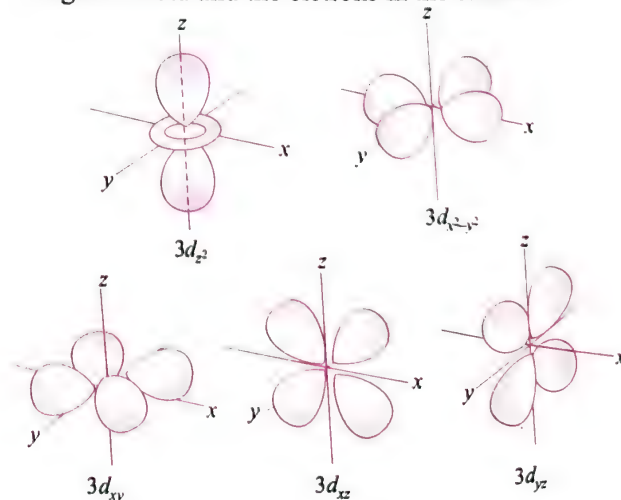


Fig. 7.28 Spatial arrangement of five d -orbitals

However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3

and $\text{H}_2\ddot{\text{O}}:$) in a complex, it becomes asymmetrical and the degeneracy of the d -orbitals is lifted. It results in the splitting of the d -orbitals. The pattern of splitting depends upon the nature of the crystal field. It is this splitting of d -orbital energies and its effects that forms the basis of crystal field theory.

In most transition metal complexes, either six or four ligands surround the metal, giving octahedral or tetrahedral structures. In both of these cases the field produced by the ligands is not spherically symmetrical thus the d -orbitals are not affected equally by the ligand field.

7.11.1 CRYSTAL FIELD SPLITTING OF d -ORBITALS IN OCTAHEDRAL COMPLEXES

- i. In an octahedral complex, the metal is at the centre of the octahedron and the ligands are at the six corners. The direction x , y and z point to three adjacent corners of the octahedron as shown in Figure 7.29.

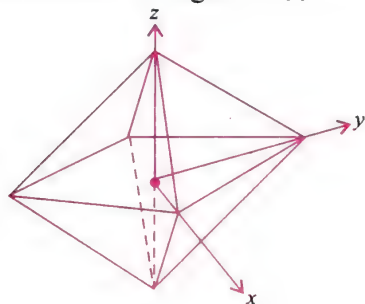


Fig. 7.29 The directions in an octahedral complex

- ii. In octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in the metal d -orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal d -orbital is directed towards the ligand than when it is away from the ligand. Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy and the d_{xy} , d_{yz} and d_{zx} orbitals which are directed between the axis will be lowered in energy relative to the average energy in the spherical crystal field (as shown in Figure 7.30).

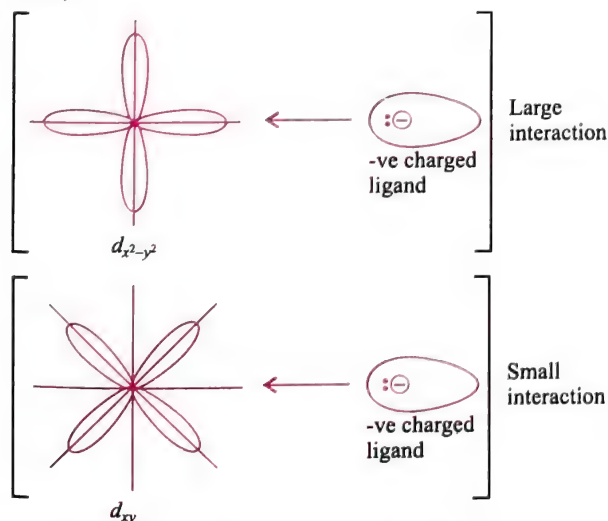


Fig. 7.30 Interaction of ligands with d -orbitals

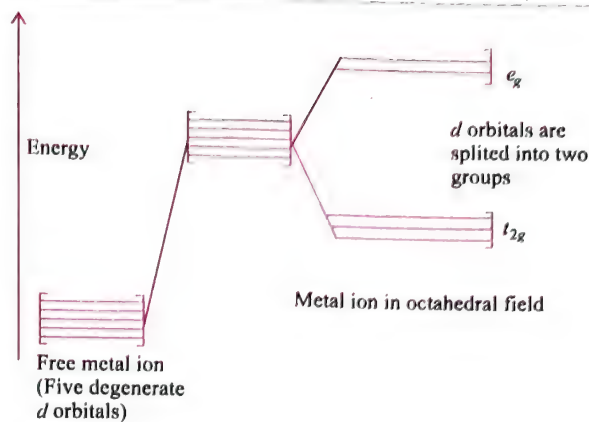


Fig. 7.31 (a) Crystal field splitting of d -orbitals in an octahedral field

Thus, the degeneracy of the d -orbitals have been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set [as shown in Figure 7.31(a) and 7.31(b)].

The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes x , y and z . The lobes of the t_{2g} orbitals (d_{xy} , d_{xz} and d_{yz}) point in between the axes. It follows that the approach of the six ligands along the x , y , z , $-x$, $-y$ and $-z$ directions will increase the energy of the orbitals $d_{x^2-y^2}$ and d_{z^2} (which point along the axes) much more than it increases the energy of the d_{xy} , d_{xz} and d_{yz} orbitals (which point between the axes).

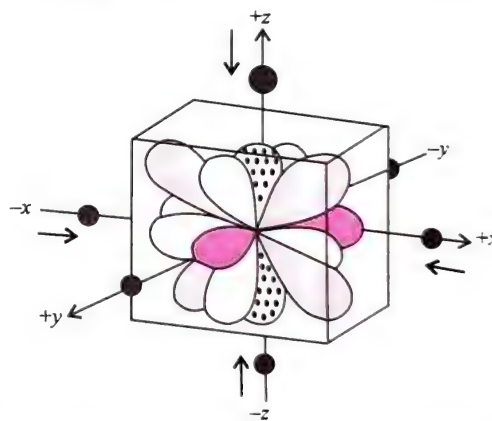


Fig. 7.31 (b) Complete set of d -orbitals in an octahedral produced by six ligands. The e_g orbitals are shaded and the t_{2g} orbitals are unshaded. The torus of the d_{z^2} orbital has been omitted for clarity

- iii. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as **crystal field splitting (CFS)** and the energy separation is denoted by Δ_0 (the subscript 0 is for octahedral). Thus, the energy of the two e_g orbitals will increase by $(\frac{3}{5}$ or 0.6) Δ_0 and that of the three t_{2g} will decrease by $(\frac{2}{5}$ or 0.4) Δ_0 . To understand this splitting more clearly we can assume it be to a two step process as shown in figure.

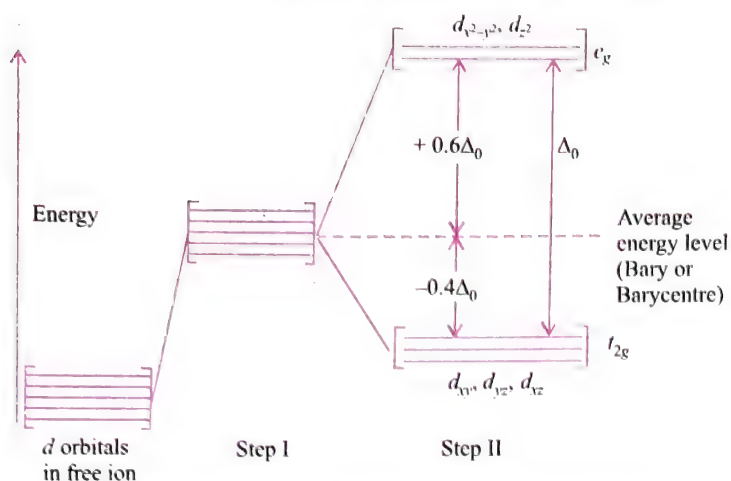


Fig. 7.32 d-orbitals splitting in an octahedral crystal field

Step 1: Average energy of the d-orbitals of metal atom/ion in a hypothetical spherical crystal field.

Step 2: Splitting of d-orbitals of metal atom/ion in octahedral crystal field.

In step 1, the ligands approach the central metal, producing a hypothetical spherical field which repels all of the d-orbitals to the same extent. In step 2, the ligands exert an octahedral field, which splits the orbital degeneracy. In going from step 1 to step 2, average energy (the barycentre or “centre of gravity”) of the orbitals must remain constant and thus, the two ‘ e_g ’ orbitals to be further repelled by $0.6 \Delta_0$ while the three ‘ t_{2g} ’ orbitals are stabilised to an extent of $0.4 \Delta_0$ as shown in figure 7.32. This constancy of the barycentre of the d-orbitals holds for all complexes, regardless of geometry.

Note: The set of d-orbitals are divided in two groups:

- The orbitals in which lobes lie on the axes ($d_{x^2-y^2}$; d_{z^2})** referred to as “ e_g ” orbitals in octahedral symmetry and “ e ” orbitals in tetrahedral symmetry. (also called as doubly degenerate orbitals). OR where ‘ e ’ stands for set of two orbitals and ‘ g ’ stands for gerade i.e. symmetrical.
- The orbitals in which lobes lie in between the axes (d_{xy} , d_{yz} , d_{zx})** referred to as “ t_{2g} ” orbitals in octahedral symmetry and “ t_2 ” orbitals in tetrahedral symmetry (also called triply degenerate orbitals). OR where “ t_{2g} ” stands for set of three orbitals (t) which are asymmetric with respect to C_2 axis perpendicular to the highest C_n axis but which is symmetric in sign (g) through the centre of inversion.

- Referring to the energy level of an isolated metal atom, the weighted mean of these two sets of degenerate orbitals is taken as zero, this is some times called the **Barycentre**. The difference in energy between the two d levels is given either of the symbols Δ_0 or $10\Delta_q$.

The size of the energy gap Δ_0 between the t_{2g} and e_g levels can be measured easily by recording the UV-visible spectrum of the complex. Consider a complex like $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, the Ti^{3+} ion has one d electron. In the complex this will occupy the orbital with the lowest energy, that is one of the t_{2g} orbitals as shown in Table. The complex absorbs light of the

correct wavelength (energy) to promote the electron from the t_{2g} level to the e_g level.

- $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ shows maximum absorption at $20,300 \text{ cm}^{-1}$. The value of Δ_0 i.e., “Crystal Field Splitting Energy” (CFSE) for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ can be calculated as

$$\begin{aligned}\Delta_0 &= E = \frac{N_A hc}{\lambda} = N_A hc \bar{\nu} \\ &= 6.023 \times 10^{23} \text{ mol}^{-1} \times 6.6 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1} \\ &\quad \times 20300 \times 10^2 \text{ m}^{-1} \\ &= 241.97 \times 103 \text{ J mol}^{-1} \\ &= 242 \text{ kJ mol}^{-1}\end{aligned}$$

Because of the crystal field splitting of d-orbitals, the single d-electron in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ occupies an energy level $0.4 \Delta_0$ below the average energy of the d-orbitals. As a result the complex is more stable. The crystal field stabilisation energy, CFSE in this case is

$$\text{CFSE} = -0.4 \Delta_0 = -0.4 \times 242 \text{ kJ mol}^{-1}$$

$$\Delta_0 = -96.8 \text{ kJ mol}^{-1}$$

7.11.2 SIGNIFICANCE OF Δ_0

Consider a d^1 coordination entity e.g. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ formed in aqueous solution of Ti^{3+} (d^1) ion, now the single d-electron occupies one of the lower energy t_{2g} orbitals. Similarly in the d^2 and d^3 coordination entities, the d-electrons will occupy the lower energy t_{2g} orbital in accordance with the Hund’s rule. For d^4 ions, two possible pattern of electron distribution arise depending upon the relative values of Δ_0 and P , where P represents the energy required for electron pairing in a single orbital called the **pairing energy**.

- If $\Delta_0 < P$ (weak field, high spin situation):** The fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$ (see Figure 7.33). If now a fifth electron is added to a weak field coordination entity, the configuration becomes $t_{2g}^3 e_g^2$.
- If $\Delta_0 > P$ (strong field, low spin situation):** Pairing will occur in the t_{2g} level with e_g level remaining unoccupied giving configuration $t_{2g}^4 e_g^0$.

Note: The pairing will occur (and consequently the e_g level will remain unoccupied) till the entities of d^6 ions.]

$$\text{CFSE} = (3 \times -0.4 + 0.6) \Delta_0 = -0.6 \Delta_0$$

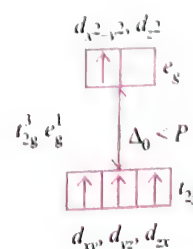


Fig. 7.33 Weak field

$$\text{CFSE} = [4 \times (-0.4)] = -1.6 \Delta_0$$

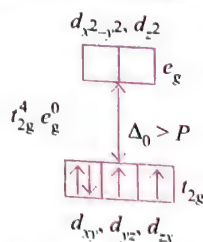


Fig. 7.34 Strong field

Note: Calculations show that coordination entities with four to seven d -electrons are more stable for strong field as compared to weak field cases.

- c. The CFSE in weak field (Fig. 7.33) is larger than in strong field (Fig. 7.34). However, the energy P used to pair the electrons must be allowed for, so the total stabilisation energy in strong field is $-1.6 \Delta_0 + P$.
- d. For a given metal ion P is constant. Thus the amount of CFSE is determined by the strength of the ligand field. A weak ligand (e.g., Cl^-) will only cause a small splitting of energy levels Δ_0 . Thus it will be more favourable energetically for electrons to occupy the upper e_g level and have a high spin complex, rather than to pair electrons. Similarly, strong field ligands (e.g., CN^-) cause a large splitting Δ_0 . In this case it requires less energy to pair the electrons to form a low spin complex.

Similar arguments apply to high and low spin complexes of metal ions with d^5 , d^6 and d^7 configuration as summarised in Table.

7.11.3 EFFECT OF CRYSTAL FIELD SPLITTING

In octahedral complexes, the filling of t_{2g} orbitals decreases the energy of a complex that makes it more stable by $-0.4 \Delta_0$ per electron.

Filling e_g orbitals increases the energy by $+0.6 \Delta_0$ per electron. The total crystal field stabilisation energy is given by

$$\text{CFSE}_{(\text{octahedral})} = [-0.4n_{(t_{2g})} + 0.6n_{(e_g)}] \Delta_0$$

where $n_{(t_{2g})}$ and $n_{(e_g)}$ are the number of electrons occupying the t_{2g} and e_g orbitals respectively. The CFSE is zero for ions with d^0 and d^{10} configurations in both strong and weak ligand fields. The CFSE is also zero for d^5 configurations in a weak field (refer to Table 7.18).

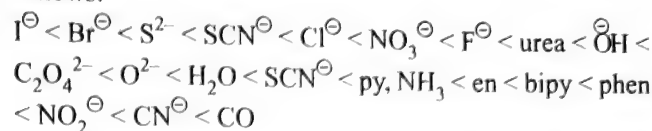
7.11.4 FACTORS AFFECTING THE MAGNITUDE OF CRYSTAL FIELD SPLITTING ENERGY

The factors affecting the magnitude of crystal field splitting energy (Δ_0) are as follows:

1. Nature of the ligands
2. Charge on the metal ion
3. Size of the metal ion

1. Nature of the ligands: Ligands which cause only a small degree of crystal field splitting are termed weak field ligands. Ligands which cause a large splitting are called

strong field ligands. The common ligands can be arranged in increasing order of crystal field splitting Δ_0 . The order remains practically constant for different metals and this series is called the **spectrochemical series**, which is as follows:



The series can be split into weak field ligands, border line and strong field ligands. [refer to section 7.10.2, Point (iv)]

The **spectrochemical series** is an experimentally determined series based on the absorption of light. It is difficult to explain the order as it incorporates both the effects of σ and π bonding. The halides are in the order expected from electrostatic effects. In other cases we must consider covalent bonding to explain the order. A pattern of increasing σ donation is follows:

Halide donors < O donors < N donors < C donors

The crystal field splitting produced by the strong field CN^- ligand is about double that for weak field ligands like the halide ions. This is attributed to π bonding in which the metal donates electrons from a filled t_{2g} orbital into a vacant orbital on the ligand. In a similar way, many unsaturated N donors and C donors may also act as π acceptors.

Ligands given in the borderline criteria act as both strong and weak field ligands. By knowing the value of magnetic moment, μ , it may be suggested that whether they act as strong and weak in a particular case. Generally, NH_3 behaves as a strong field ligand and H_2O as weak field ligand. The compound $[\text{Co}(\text{OX})_3]^{3-}$ is one of few rare examples where oxalate ion acts as strong field ligand.

- 2. Charge on the metal ion:** The magnitude of Δ_0 increases as the charge on the central ion increases.

As the charge on the central atom increases, its interaction with the ligands increases, thereby leading to an increase in value of Δ_0 .

It has been observed that for the first row transition metal ions, the values of Δ_0 for M^{2+} complexes are roughly 50% larger than the values of M^{3+} complexes.

- 3. Size of the metal ion:** The value of Δ_0 increases by about 30% between adjacent members down a group of first (3d), second (4d), third (5d) series of transition elements in the order $3d < 4d < 5d$.

As the size of the central atom/ion in the complex increases, its interaction with the ligands increases which leads to an increase in the value of Δ_0 .

7.11.5 CFSE AND ELECTRONIC CONFIGURATION IN OCTAHEDRAL COMPLEX

Table 7.18 shows CFSE and electronic arrangement in octahedral complex.

Table 7.18 CFSE and electronic arrangement in octahedral complex

Electronic configuration	Octahedral	n	CFSE Δ_0	Spin only magnetic moment μ_s (D) = $\sqrt{n(n+2)}$ BM
d^1	$\begin{array}{c} \text{--- } e_g \\ 1 \text{--- } t_{2g} \end{array}$	1	$-0.4 \times 1 = -0.4$	$\sqrt{3} = 1.73$
d^2	$\begin{array}{c} \text{--- } e_g \\ 11 \text{--- } t_{2g} \end{array}$	2	$-0.4 \times 2 = -0.8$	$\sqrt{8} = 2.83$
d^3	$\begin{array}{c} \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	3	$-0.4 \times 3 = -1.2$	$\sqrt{15} = 3.87$
d^4	WF $\begin{array}{c} 1 \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	4	$-0.4 \times 3 + 0.6 \times 1 = -0.6$	$\sqrt{24} = 4.90$
	SF $\begin{array}{c} \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	2	$-0.4 \times 4 = -1.6$	$\sqrt{8} = 2.83$
d^5	WF $\begin{array}{c} 11 \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	5	$-0.4 \times 3 + 0.6 \times 2 = -0.0$	$\sqrt{35} = 5.92$
	SF $\begin{array}{c} \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	1	$-0.4 \times 5 = -2.0$	$\sqrt{3} = 1.73$
d^6	WF $\begin{array}{c} 11 \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	4	$-0.4 \times 4 + 0.6 \times 2 = -0.4$	$\sqrt{24} = 4.90$
	SF $\begin{array}{c} \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	0	$-0.4 \times 6 = -2.4$	0.00
d^7	WF $\begin{array}{c} 11 \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	3	$-0.4 \times 5 + 0.6 \times 2 = -0.8$	$\sqrt{15} = 3.87$
	SF $\begin{array}{c} 1 \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	1	$-0.4 \times 6 + 0.6 \times 1 = -1.8$	$\sqrt{3} = 1.73$
d^8	Both WF and SF $\begin{array}{c} 11 \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	2	$-0.4 \times 6 + 0.6 \times 2 = -1.2$	$\sqrt{8} = 2.83$

d^9	Both WF and SF $\begin{array}{c} 11 \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	1	$-0.4 \times 6 + 0.6 \times 3 = -0.6$	$\sqrt{3} = 1.73$
d^{10}	Both WF and SF $\begin{array}{c} 11 \text{--- } e_g \\ 111 \text{--- } t_{2g} \end{array}$	0	$-0.4 \times 6 + 0.6 \times 4 = -0.00$	0.00

Note: Symbols used: OH = octahedral complexes, WF = The configuration for high spin and weak field complexes, SF = The configuration for low spin and strong field complexes, n = Number of unpaired electrons.

ILLUSTRATION 7.46

Prove that the lowering of the stabilised orbitals is $0.4 \Delta_0$ while the raising of the destabilised orbitals is $0.6 \Delta_0$.

Sol. The total energy of separation is Δ_0 . Let x = energy of stabilisation and y = energy of destabilisation. Then $y - x = \Delta_0$. Since the orbitals yield no net increase in energy when they are equally occupied.

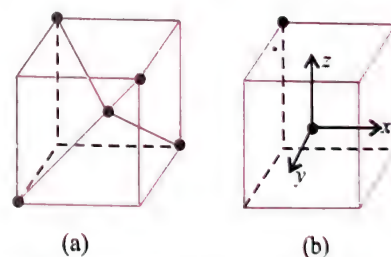
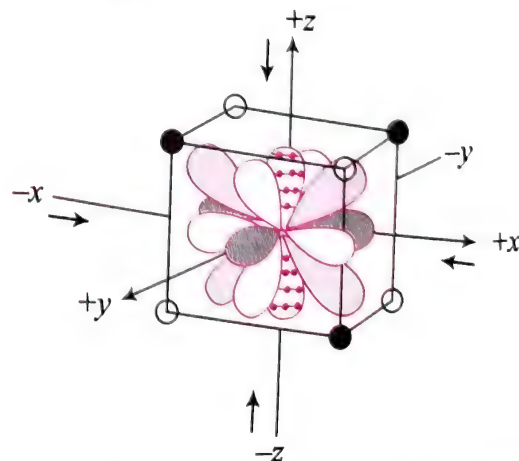
$$\therefore 3x + 2y = 0$$

$$\Rightarrow 3x + 2(\Delta_0 + x) = 0$$

$$\therefore 5x = -2\Delta_0 \quad x = -0.4 \Delta_0 \quad \text{and} \quad y = +0.6 \Delta_0$$

7.11.6 CFSE OF d -ORBITALS IN TETRAHEDRAL COMPLEXES

A regularly tetrahedron is related to a cube. One atom is at the centre of the cube, and four of the eight corners of the cube are occupied by ligands as shown in Figures 7.35 and 7.36.

**Fig. 7.35** Relation of a tetrahedron to a cube**Fig. 7.36** Complete set of d -orbitals in a cubic field. Either set of tetrahedral ligands (\bullet or \circ) produces a field one-half as strong as the cubic field

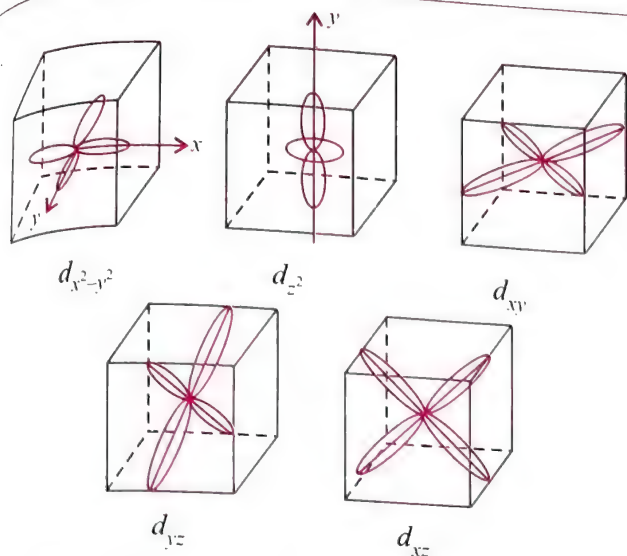


Fig. 7.37 Orientation of a orbitals relative to a cube

The direction x , y and z point to the centres of the faces of the cube. The orbitals d_{xy} , d_{xz} and d_{yz} point along x , y and z (that is to the centres of the faces). The orbitals $d_{x^2-y^2}$ and d_{z^2} point between x , y and z (that is towards the centres of the edges of the cube) (as shown in Fig. 7.37).

The ligands do not directly approach any of the metal d -orbitals, but they come closer to the orbitals directed to the edges of the cube (d_{xy} , d_{yz} and d_{xz}) than to those directed to the centres of the cube faces ($d_{x^2-y^2}$ and d_{z^2}).

The angle between any of d_{xy} , d_{yz} and d_{xz} orbital, the central metal and the ligand is half the tetrahedral angle $= 109^\circ 28' / 2 = 54^\circ 44'$.

The angle between $d_{x^2-y^2}$ and d_{z^2} orbital, the central metal and the ligand is $35^\circ 16'$.

The approach of the ligands raises the energy of both sets of orbitals. The energy of d_{xy} , d_{yz} and d_{xz} set of orbitals is raised more because they are closer to the ligands. This crystal field splitting is the opposite way round to that in the octahedral complexes as shown in Fig. 7.38.

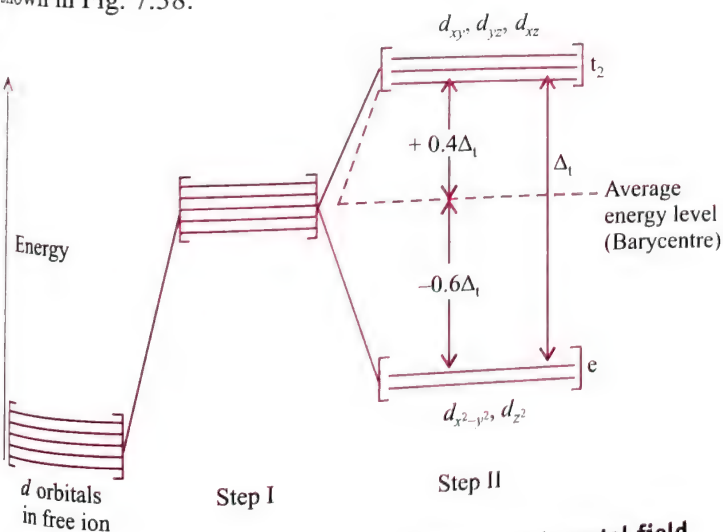


Fig. 7.38 d-orbitals splitting in a tetrahedral crystal field

Step I: Average energy of the d -orbitals of metal atom/ion in a hypothetical spherical crystal field.

Step II: Splitting of d -orbitals of metal atom/ion in tetrahedral crystal field.

Note: In tetrahedral complexes, mostly $\Delta_t < P$ ($\Delta_t \equiv 4/9 \Delta_o$) and hence they generally form high spin complexes.

The labels we apply to the two sets of degenerate orbitals are consistent with their symmetry properties in a tetrahedral environment: ' t_2 ' for d_{xy} , d_{yz} and d_{xz} orbitals and ' e ' for the $d_{x^2-y^2}$ and d_{z^2} orbitals. The ' g ' subscript which was used for the octahedral field is no longer appropriate because the tetrahedron lacks a centre of inversion.

The ' t_2 ' orbitals are $0.4 \Delta_t$ above the weighted average energy of the two groups (the Barycentre) and the ' e ' orbitals are $0.6 \Delta_t$ below the average.

The magnitude of the crystal field splitting Δ_t in tetrahedral complexes is considerably less than in octahedral field. There are two reasons for this:

1. There are only four ligands instead of six, so the ligand field is only two thirds the size, hence the ligand field splitting is also two thirds the size.
2. The direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly a further two thirds.

Thus the tetrahedral crystal field splitting Δ_t is roughly $2/3 \times 2/3 = 4/9$ of the octahedral crystal field splitting Δ_o . Strong field ligands cause a bigger energy difference between ' t_2 ' and ' e ' than weak field ligands. However, the tetrahedral splitting Δ_t is always much smaller than the octahedral splitting Δ_o . Thus it is never energetically favourable to pair electrons, **and almost all tetrahedral complexes are high-spin and low-spin tetrahedral complexes are rarely observed.** One such example of low spin tetrahedral complexes of first row transition metal is tetrakis (1-norbornyl) cobalt (IV). Rather, under conditions favouring strong crystal fields, other geometries are preferred over tetrahedral structures.

7.11.7 TOTAL CRYSTAL FIELD STABILISATION ENERGY

$CFSE_{(tetrahedral)} = [-0.6 n_{(e)} + 0.4 n_{(t_2)}] \Delta_t$ where $n_{(e)}$ and $n_{(t_2)}$ are the number of electrons occupying the ' e ' and ' t_2 ' orbitals respectively. The $CFSE_{(TH)}$ is zero for ions with d^0 , d^5 and d^{10} configuration in both strong and weak ligand field (Refer to Table 7.19).

7.11.8 CFSE IN BOTH OCTAHEDRAL AND TETRAHEDRAL COMPLEXES

This shows that for d^0 , d^5 and d^{10} arrangements the CFSE is zero in both octahedral and tetrahedral complexes (refer Tables 7.16 and 7.17). For all other electronic arrangements there is some CFSE and the octahedral CFSE is greater than the tetrahedral CFSE. It follows that octahedral complexes are generally more stable and more common than tetrahedral complexes. This is partly because there are six bond energy terms rather than four and partly because there is a larger CFSE term. Despite this some tetrahedral complexes are formed and are stable. Tetrahedral complexes are favoured:

1. Where the ligands are large and bulky and could cause crowding in an octahedral complex.
2. Where attainment of a regular shape is important. For tetrahedral complexes d^0 , d^2 , d^5 , d^7 and d^{10} configurations are regular. Some tetrahedral complexes which are regular are:

$\text{Ti}^{\text{IV}}\text{Cl}_4(e^0, t_2^0)$, $[\text{Mn}^{\text{VII}}\text{O}_4]^\ominus(e^0, t_2^0)$, $[\text{Fe}^{\text{VI}}\text{O}_4]^{2-}(e^0, t_2^0)$, $[\text{Fe}^{\text{III}}\text{Cl}_4]^\ominus(e^2, t_2^3)$, $[\text{Co}^{\text{II}}\text{Cl}_4]^{2-}(e^4, t_2^3)$ and $[\text{Zn}^{\text{II}}\text{Cl}_4]^{2-}(e^4, t_2^6)$

- When the ligands are weak field, and the loss in CFSE is thus less important.
- Where the central metal has a low oxidation state. This reduces the magnitude of Δ .
- Where the electronic configuration of the central metal is d^0 , d^5 or d^{10} as there is no CFSE.
- Where the loss of CFSE is small, e.g. d^1 and d^6 where the loss in CFSE is $0.27\Delta_0$ or d^2 and d^7 where the loss is $0.53\Delta_0$.
- Many transition metal chlorides, bromides and iodides form tetrahedral structures.

7.11.8.1 Comparison of CFSE and Electronic Arrangement in Tetrahedral (TH) and Octahedral (OH) Complexes

Table 7.19 CFSE and electronic arrangement in TH and OH complexes

Con-fig-ur-ation	Arrangement of electrons in TH complexes	n & μ_{spin} BM	CFSE (Δ_t)	TH (CFSE) scaled for comparison with OH assuming ($\Delta_t = 4/9\Delta_0$)
d^1	$\text{---}t_2$ $1\text{---}e$	1 1.73	-0.6×1 $= -0.6$	$-0.6 \times 4/9$ $= -0.27\Delta_0$
d^2	$\text{---}t_2$ $11\text{---}e$	2 2.83	-0.6×2 $= -1.2$	$-1.2 \times 4/9$ $= -0.53\Delta_0$
d^3	$1\text{---}t_2$ $11\text{---}e$	3 3.87	$-0.6 \times 2 + 0.4$ $= -0.8$	$-0.8 \times 4/9$ $= -0.36\Delta_0$
d^4	$11\text{---}t_2$ $11\text{---}e$	4 4.90	$-0.6 \times 2 + 0.4 \times 2$ $= -0.4$	$-0.4 \times 4/9$ $= -0.18\Delta_0$
d^5	$111\text{---}t_2$ $11\text{---}e$	5 5.92	$-0.6 \times 2 + 0.4 \times 3$ $= 0.0$	$-0.0 \times 4/9$ $= 0.00$
d^6	$111\text{---}t_2$ $11\text{---}e$	4 4.90	$-0.6 \times 3 + 0.4 \times 3$ $= -0.6$	$-0.6 \times 4/9$ $= -0.27\Delta_0$
d^7	$111\text{---}t_2$ $11\text{---}e$	3 3.87	$-0.6 \times 4 + 0.4 \times 3$ $= -1.2$	$-1.2 \times 4/9$ $= -0.53\Delta_0$
d^8	$111\text{---}t_2$ $11\text{---}e$	2 2.83	$-0.6 \times 4 + 0.4 \times 4$ $= -0.8$	$-0.8 \times 4/9$ $= -0.36\Delta_0$
d^9	$111\text{---}t_2$ $11\text{---}e$	1 1.73	$-0.6 \times 4 + 0.4 \times 5$ $= -0.4$	$-0.4 \times 4/9$ $= -0.18\Delta_0$

d^{10}	$111\text{---}t_2$ $11\text{---}e$	0 0.00	$-0.6 \times 4 + 0.4 \times 6$ $= 0.0$	$-0.0 \times 4/9$ $= 0.00$
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7.11.9 CFSE OF d-ORBITAL IN SQUARE PLANAR COMPLEXES

The square planar geometry may be considered to be derived from octahedral by removing the two ligands which were approaching the central atom along the Z-axis (called tetragonal distortion).

The splitting may also be explained as the lobes of $d_{x^2-y^2}$ point towards the ligands, this orbital has highest energy.

Though lobes of d_{xy} orbital lie between the ligands but they are coplanar with them, hence this orbital is next higher in energy. The lobes of d_{z^2} orbital point out of the plane of the complex but the torus around its centre lies in the plane, therefore d_{z^2} orbital is next higher in energy. The lobes of d_{xz} and d_{yz} orbitals point out of the plane of the complex, hence they are least affected by the electrostatic field of the ligands, and thus have lowest but equal energy. The average energy of the orbitals remains constant in this redistribution of energy as in octahedral and tetrahedral complexes (the stronger the surrounding field, the higher the $d_{x^2-y^2}$ orbital will be raised, however the lower, occupied orbitals will drop in energy by a corresponding amount) (Fig. 7.39).

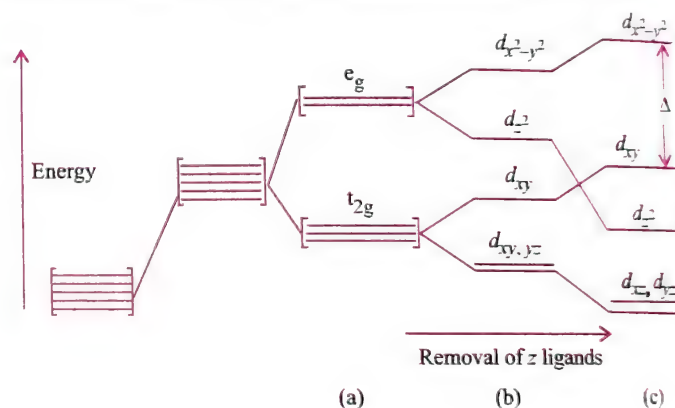


Fig. 7.39 d-orbitals splitting in a square planar field
(a) An octahedral complex undergoing z-axis elongation
(b) It becomes tetragonally distorted and
(c) Finally reaches the square planar limit

Note: The d_{z^2} orbitals may lie below the e_g (d_{xz} and d_{yz}) orbitals in the square planar complex.

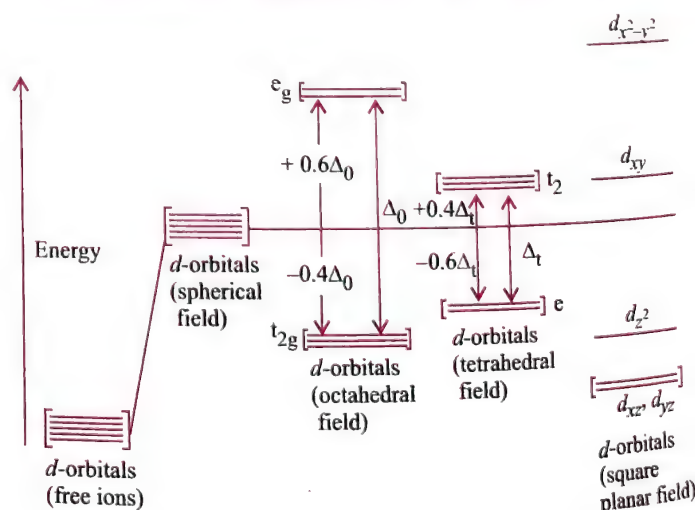
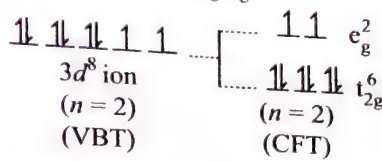
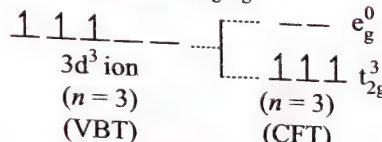
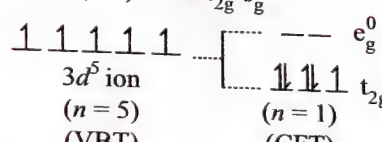
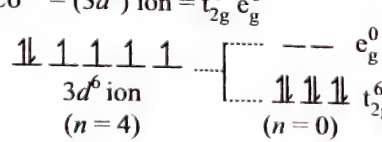
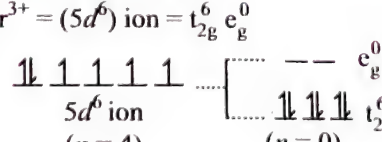
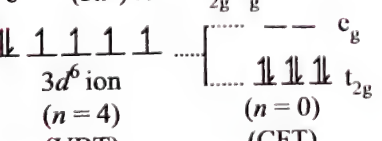


Fig. 7.40 Comparison of crystal field splitting in all three fields

The square planar geometry is favoured by metal ions having a d^8 configuration in the presence of a strong field. This combination gives low spin complexes with the eight d-electrons occupying the low energy d_{xz} , d_{yz} , d_{z^2} and d_{xy} orbitals, while the high-energy orbitals remains unoccupied.

7.11.10 COMPARISON BETWEEN THE ENERGY LEVEL DIAGRAM, ELECTRONIC CONFIGURATION AND μ_{spin} VALUES OF SOME COMPLEXES BY VBT AND CFT

Table 7.20 Based on VBT and CFT, the energy level diagram, electronic configuration of the central metal atom/ion and μ_{spin} values of some of the complexes

S.No.	Complexes	Electronic configuration diagram	No. of unpaired electrons (n) by CFT	μ_{spin} (BM)
1.	$[\text{Ni}(\text{NH}_3)_6]^{2+}$ strong field ligand CN = 6 Octahedral	$\text{Ni}(Z = 27) = 3d^8 4s^2$ $\text{Ni}^{2+} = (3d^8) \text{ ion} = t_{2g}^6 e_g^2$ 	2	$\sqrt{8} = 2.82$
2.	$[\text{Cr}(\text{CN})_6]^{3-}$ strong field ligand CN = 6 Octahedral	$\text{Cr}(Z = 24) = 3d^5 4s^1$ $\text{Cr}^{3+} = (3d^3) \text{ ion} = t_{2g}^3 e_g^0$ 	3	$\sqrt{15} = 3.87$
3.	$[\text{Mn}(\text{CN})_6]^{4-}$ CN^- strong field ligand, pairing in ' t_{2g} ' orbital occurs CN = 6 Octahedral	$\text{Mn}(Z = 25) = 3d^5 4s^2$ $\text{Mn}^{2+} = (3d^5) \text{ ion} = t_{2g}^5 e_g^0$ 	1	$\sqrt{3} = 1.73$
4.	$[\text{Co}(\text{CN})_6]^{3-}$ strong field ligand, pairing in ' t_{2g} ' orbital occurs	$\text{Co}(Z = 27) = 3d^7 4s^2$ $\text{Co}^{3+} = (3d^6) \text{ ion} = t_{2g}^6 e_g^0$ 	0	0
5.	$[\text{Ir}(\text{NH}_3)_6]^{3+}$ strong field ligand, pairing in ' t_{2g} ' orbital occurs Note: High nuclear charge on metal of lower transition (i.e., 4d or 5d) series always forms low spin inner orbital complex irrespective of nature of ligand.	$\text{Ir}(Z = 77) = 5d^7 6s^2$ $\text{Ir}^{3+} = (5d^6) \text{ ion} = t_{2g}^6 e_g^0$ 	0	0
6.	$[\text{Fe}(\text{CN})_6]^{4-}$ strong field ligand	$\text{Fe}(Z = 26) = 3d^6 4s^2$ $\text{Fe}^{2+} = (3d^6) \text{ ion} = t_{2g}^6 e_g^0$ 	0	0

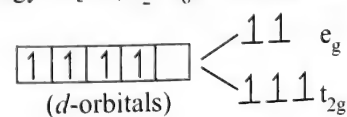
7.	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ weak field ligand	$\text{Fe}(Z = 26) = 3d^6 4s^2$ $\text{Fe}^{2+} = (3d^6) \text{ ion} = t_{2g}^4 e_g^2$ $\begin{array}{c} \uparrow\downarrow \uparrow \uparrow \uparrow \uparrow \\ 3d^6 \text{ ion} \\ (n = 4) \\ \text{(VBT)} \end{array} \quad \begin{array}{c} \begin{array}{c} \uparrow\uparrow \\ \uparrow\downarrow \uparrow \end{array} e_g^2 \\ t_{2g}^4 \end{array}$	4	$\sqrt{24} = 4.898$
8.	$[\text{IrCl}_6]^{3-}$ In 3rd transition element series, Δ_0 is so large that it becomes greater than P (pairing energy) ($P < \Delta_0$). Cl^- acts as strong field ligand and thus pairing of '2g' orbital occurs	$\text{Ir}(Z = 77) = 5d^7 6s^2$ $\text{Ir}^{3+} = (5d^6) \text{ ion} = t_{2g}^6 e_g^0$ $\begin{array}{c} \uparrow\downarrow \uparrow \uparrow \uparrow \uparrow \\ 5d^6 \text{ ion} \\ (n = 4) \\ \text{(VBT)} \end{array} \quad \begin{array}{c} \text{---} e_g^0 \\ \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow t_{2g}^6 \end{array}$	0	0
9.	$[\text{PtCl}_6]^{2-}$ Pt is in 5d transition element series, so ($P < \Delta_0$) Cl^- is strong field ligand as explained above in point (8)	$\text{Pt}(Z = 78) = 5d^9 6s^1$ $\text{Pt}^{4+} = (5d^6) \text{ ion} = t_{2g}^6 e_g^0$ $\begin{array}{c} \uparrow\downarrow \uparrow \uparrow \uparrow \uparrow \\ 5d^6 \text{ ion} \\ (n = 4) \\ \text{(VBT)} \end{array} \quad \begin{array}{c} \text{---} e_g^0 \\ \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow t_{2g}^6 \end{array}$	0	0
10.	$[\text{Rh}(\text{NH}_3)_6]^{3+}$ Strong field ligand Rh is in 2nd transition element series	$\text{Rh}(Z = 45) = 4d^8 5s^1$ $\text{Rh}^{3+} = (4d^6) \text{ ion} = t_{2g}^6 e_g^0$ $\begin{array}{c} \uparrow\downarrow \uparrow \uparrow \uparrow \uparrow \\ 4d^6 \text{ ion} \\ (n = 4) \\ \text{(VBT)} \end{array} \quad \begin{array}{c} \text{---} e_g^0 \\ \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow t_{2g}^6 \end{array}$	0	0
11.	$[\text{Mn}(\text{CN})_6]^{3-}$ Strong field ligand	$\text{Mn}(Z = 25) = 3d^5 4s^2$ $\text{Mn}^{3+} = (3d^4) \text{ ion} = t_{2g}^4 e_g^0$ $\begin{array}{c} \uparrow \uparrow \uparrow \uparrow \text{---} \\ 3d^4 \text{ ion} \\ (n = 4) \text{ (VBT)} \end{array} \quad \begin{array}{c} \text{---} e_g^0 \\ \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow t_{2g}^4 \end{array}$	2	$\sqrt{8} = 2.828$
12.	$[\text{CoF}_6]^{4-}$ Weak field ligand	$\text{Co}(Z = 25) = 3d^7 4s^2$ $\text{Co}^{2+} = (3d^7) \text{ ion} = t_{2g}^5 e_g^2$ $\begin{array}{c} \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \uparrow \\ 3d^7 \text{ ion} \\ (n = 3) \\ \text{(VBT)} \end{array} \quad \begin{array}{c} \uparrow\uparrow e_g^2 \\ \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow t_{2g}^5 \end{array}$	2	$\sqrt{8} = 2.828$

ILLUSTRATION 7.47

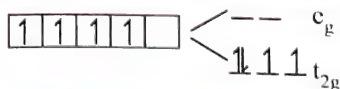
For the complex $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, calculate the total pairing energy in high spin and low spin state. Given the mean pairing energy = 23500 cm^{-1} .

Sol. In complex $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, oxidation state of Cr is +2, i.e. Cr^{2+} is present which has $3d^4$ configuration. The configuration

of d^4 ion in high spin state is $t_{2g}^3 e_g^1$, since no electron is paired. total pairing energy of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ in high spin state is $0 \times P = 0$.



The configuration of d^4 ion in low spin state is $t_{2g}^4 e_g^0$, since pairing of an electron takes place, total pairing energy of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ in low spin state is $1 \times P = 1 \times 23500 \text{ cm}^{-1} = 23500 \text{ cm}^{-1}$.

**ILLUSTRATION 7.48**

Which complex of the following pairs has the larger value of Δ_0 .

- $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$
- $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{CoF}_6]^{3-}$
- $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$

Sol.

- $[\text{Co}(\text{CN})_6]^{3-}$ has larger value of Δ_0 than $[\text{Co}(\text{NH}_3)_6]^{3+}$, since CN^- has greater field strength than NH_3 .
- NH_3 has greater field strength than F^- ion, hence Δ_0 will be greater for $[\text{Co}(\text{NH}_3)_6]^{3+}$.
- Charge on Co in $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is +2, whereas charge on Co in $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is +3. Since charge on $[\text{Co}(\text{NH}_3)_6]^{3+}$ is higher than $[\text{Co}(\text{NH}_3)_6]^{2+}$, Δ_0 for $[\text{Co}(\text{NH}_3)_6]^{3+}$ is larger than $[\text{Co}(\text{NH}_3)_6]^{2+}$.

ILLUSTRATION 7.49

For Mn^{3+} ion, the electron pairing energy, P is 28000 cm^{-1} , Δ_0 values for the complexes $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Mn}(\text{CN})_6]^{3-}$ are 21000 cm^{-1} and 38500 cm^{-1} respectively. Do these complexes have high spin or low spin complexes? Also write the configurations corresponding to these states.

Sol. For $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ ion, $\Delta_0 < P$ ($\Delta_0 = 21000 \text{ cm}^{-1}$, $P = 28000 \text{ cm}^{-1}$). Hence this is a high spin complex (pairing up of electron will not take place). Mn in $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ is present as Mn^{3+} ion. Mn^{3+} ion is d^4 system, its configuration is $t_{2g}^3 e_g^1$.

For $[\text{Mn}(\text{CN})_6]^{3-}$ ion $\therefore \Delta_0 > P$ ($\Delta_0 = 38500 \text{ cm}^{-1}$, $P = 28500 \text{ cm}^{-1}$). Hence pairing of electron will take place and the $[\text{Mn}(\text{CN})_6]^{3-}$ is low spin complex. Mn in $[\text{Mn}(\text{CN})_6]^{3-}$ is present as Mn^{3+} ion which is d^4 system, its configuration is $t_{2g}^4 e_g^0$.

ILLUSTRATION 7.50

For $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion, the mean pairing energy P is found to be 23500 cm^{-1} . The magnitude of Δ_0 is 13900 cm^{-1} . Calculate the crystal field stabilisation energy for the complex in configurations corresponding to high spin and low spin states. Which is more stable?

Sol. In $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion, Cr is present as Cr^{2+} ion. Electronic configuration of Cr^{2+} ion is $3d^4$, Cr^{2+} ion in high spin states: $t_{2g}^3 e_g^1$.

$$\begin{aligned} \text{CFSE} &= -3 \times 0.4 \Delta_0 + 1 \times 0.6 \Delta_0 \\ &= -1.2 + 0.6 \Delta_0 = -0.6 \Delta_0 = -0.6 \times 13900 \text{ cm}^{-1} \\ &= -8340 \text{ cm}^{-1} \end{aligned}$$

Cr^{2+} ion in low spin state: $t_{2g}^4 e_g^0$

$$\begin{aligned} \text{CFSE} &= -4 \times 0.4 \Delta_0 + P \\ &= -(1.6 \times 13900 + 23500) \text{ cm}^{-1} \\ &= (-22240 + 23500) \text{ cm}^{-1} = +1260 \text{ cm}^{-1} \end{aligned}$$

CFSE for high spin state is greater than CFSE for low spin state,

hence high spin state is more stable.

ILLUSTRATION 7.51

Give reason for the fact that crystal field theory is not applied to complexes of many group metals.

Sol. Main group metals do not have incomplete d subshells, rather they have empty or completely filled d subshells. For empty or completely filled d-subshells, $\Delta = 0$, hence crystal field theory is not applied to complexes of main group metals.

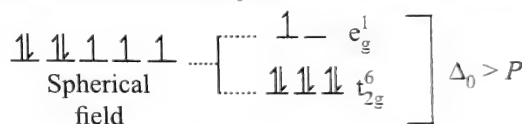
ILLUSTRATION 7.52

- Using CFT, depict the electronic configuration of the rhodium ion (Rh^{2+}) in an octahedral field for which the crystal field splitting Δ_0 is greater than the pairing energy P .
- Calculate the crystal field stabilisation energy for this configuration (in terms of Δ and P)

Sol.

$$\text{a. Rh } (Z = 45) \Rightarrow 4d^8 5s^1, \text{Rh}^{2+} = 4d^7$$

Rh^{2+} ion in octahedral field has configuration $t_{2g}^6 e_g^1$ when crystal field splitting Δ_0 is greater than the pairing energy P .



- For Rh^{2+} ion, in octahedral field ($\Delta_0 > P$).

$$\begin{aligned} \text{CFSE} &= -(0.4 \times 6) \Delta_0 + (0.6 \times 1) \Delta_0 + P \\ &= -2.4 \Delta_0 + 0.6 \Delta_0 + P = -1.8 \Delta_0 + P \end{aligned}$$

(Even in a spherical field, the complex must have two pairs of electrons, one additional pair is formed in the octahedral field)

ILLUSTRATION 7.53

What factor determines whether the crystal field in an octahedral complex is to be regarded as strong or weak? How many d-electrons must be present in orbitals of the central atom for there to be an abrupt change in crystal field stabilisation energy between strong and weak fields?

Sol. Crystal field in an octahedral complex, to be regarded as strong or weak, depends on the relative magnitude of Δ_0 and P .

- If $\Delta_0 > P$, Strong field

- If $\Delta_0 < P$, Weak field

Abrupt changes in crystal field stabilisation energy between strong and weak fields occur with d^1 , d^5 , d^6 and d^7 configurations.

7.11.11 APPLICATIONS OF CFT

Crystal field theory (CFT) is successful in explaining:

- Stability of the different stereochemical arrangements observed in different complexes.
- Spectral properties of complexes involving $d-d$ transition.
- Distortion from the symmetrical geometries with certain limitations.
- Magnetic properties of coordination compounds.

7.11.12 LIMITATIONS OF CFT

Crystal field theory is not very clear about the following:

- The spectrochemical series:** CFT assumes the interaction between central metal atom/ion and ligands in the complex to be electrostatic and therefore the anionic ligands should give maximum crystal field splitting. The reverse has been found to be true, i.e. halides (X^{\ominus}) are at the bottom of spectrochemical series (weak field ligands), OH^{\ominus} , a strong base gives a field which is weaker than H_2O (neutral ligand and have a larger size).
- The radial wave functions of the d-orbitals and of the ligands should have some overlap at the observed internuclear distances in the metal complexes. The ligands therefore are not point charges, but have their own electron orbitals.
- The CFT cannot account for the π -bonding in the complexes.
- CFT cannot explain the charge transfer spectra and the intensities of the absorption bands. These are some of the limitations of CFT, which are explained by ligand field theory (LFT).

7.12 JAHN-TELLER EFFECT AND DISTORTION IN OCTAHEDRAL AND TETRAHEDRAL COMPLEXES

Distorted Octahedral Complexes

In an octahedral complex all the six $M-L$ (L = ligand and M = central metal atom) bond lengths are equivalent. If $M-L$ bonds are of unequal lengths, the octahedral geometry of the complex gets **distorted** and we get **distorted octahedral complex**.

7.12.1 TYPES OF DISTORTED OCTAHEDRAL COMPLEXES

- Tetragonally elongated distorted octahedral complexes:** (Also see Fig. 7.41). These complexes are also called simply by the name tetragonally distorted octahedral complexes. In an octahedral complex, if the two trans or axial ligands (L_a) are moved away from the central metal atom, the distances of these two ligands from the metal atom becomes larger than that of each of the remaining four coplanar equatorial ligands (L_e) from the central metal atom. Thus the two trans bonds (also called axial bonds) or metal-ligand bonds along $+z$ and $-z$ axes become longer than each of the four equatorial bonds (equatorial) bonds are metal-ligand bonds along $+x$, $-x$, $+y$ and $-y$ axes in xy plane. The *trans* bonds become longer because these bonds are weaker than the equatorial bonds. Such octahedral complexes in which the two trans ligands are longer than each of the four equatorial bonds are called *tetragonally elongated distorted octahedral complexes* or simply *tetragonally distorted octahedral complexes* (See Fig. 7.41). The distortion which gives tetragonally distorted octahedral complex is called *tetragonal elongation distortion*.

- Square planar complexes:** (Also see Fig. 7.41). Some times the tetragonal elongation distortion in tetragonally elongated octahedral complexes is so large that the two trans ligands on z -axis are completely removed and hence octahedral complex adopt square planar geometry. For example square

planar complexes of $Cu(II)$ are highly distorted octahedral complexes.

- Tetragonally compressed distorted octahedral complexes.** (Also see Fig. 7.41). In an octahedral complex, if the two *trans* ligands are brought nearer to the central metal atom, the distance of these two *trans* ligands from the metal atom becomes shorter than that of each of the remaining four equatorial ligands from the central metal atom. Thus the two *trans* ligands become shorter than each of the four equatorial bonds. The two *trans* ligands become shorter because these bonds are stronger than the equatorial bonds. Such octahedral complexes in which the two *trans* ligands are shorter than each of the four equatorial bonds are called *tetragonally compressed (or contracted) distorted octahedral complexes*. The distortion which gives tetragonally compressed distorted octahedral complex is called *tetragonal contraction distortion*.

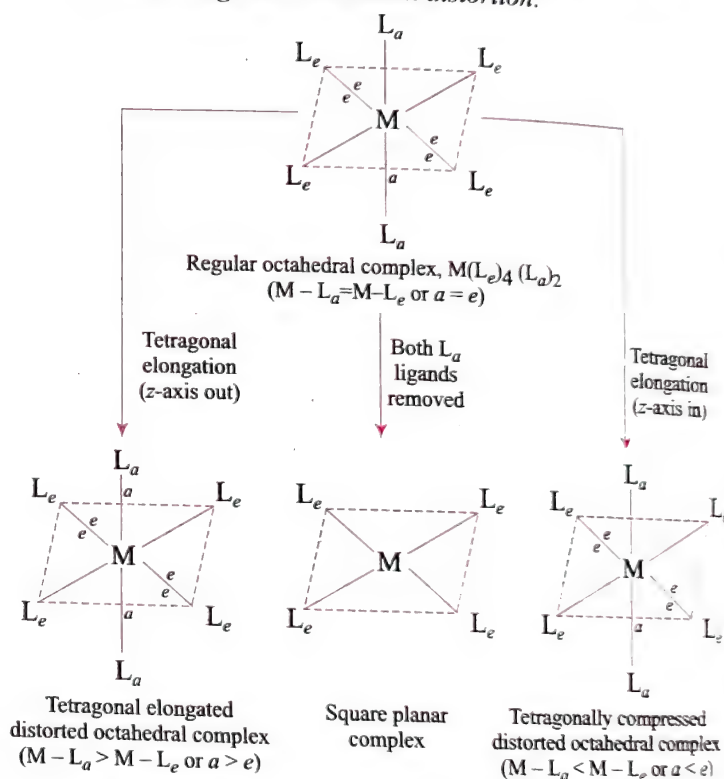


Fig. 7.41 Different types of distorted octahedral complexes

- Trigonally distorted octahedral complexes: Trigonal prismatic complexes:** When an axis passing through the centres of the two opposite triangular faces of an octahedron is increased (elongation) or decreased (compression or contraction) in length, octahedral complex gets distorted and assumes **trigonal prismatic geometry** (See Fig. 7.42).

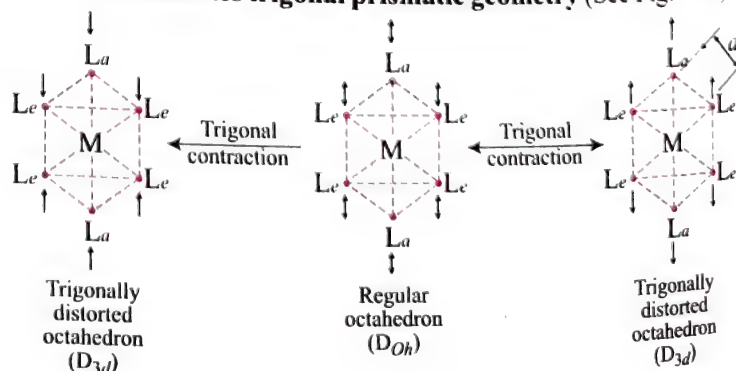


Fig. 7.42 Trigonal distortion in an octahedral ML_6 complex

7.12.2 TYPES OF DISTORTION IN OCTAHEDRAL COMPLEXES

The foregoing discussion clearly shows that the octahedral complexes can undergo the following types of distortion.

- (i) **Tetragonal distortion.** This distortion is of the following two types:
 - (a) Tetragonal elongation distortion
 - (b) Tetragonal contraction (or compression) distortion.
- (ii) Trigonal distortion
- (iii) Rhombic distortion.

7.12.2.1 Symmetrically and Asymmetrically (Unsymmetrically) Filled t_{2g} and e_g Sets of Orbitals

If t_{2g} set of orbitals (i.e., d_{xy} , d_{yz} and d_{zx} orbitals) contains 0 (empty, t_{2g}^0), 3 (half-filled, t_{2g}^3) or 6 (completely-filled, t_{2g}^6) electrons, the arrangement (distribution) of these electrons in this set is said to be symmetrical arrangement and t_{2g} set of orbitals is said to be symmetrically-filled. On the other hand, if t_{2g} set contain 1, 2, 4 or 5 electrons, the arrangement of these electrons is said to be asymmetrical arrangement and t_{2g} set of orbitals is said to be asymmetrically filled. Thus:

- (i) t_{2g}^0 (empty), t_{2g}^3 (half-filled), t_{2g}^6 (completely-filled)... symmetrically filled orbitals.
- (ii) $t_{2g}^1, t_{2g}^2, t_{2g}^4, t_{2g}^5, \dots$ asymmetrically-filled orbitals.

If e_g set of orbitals (i.e., $d_{x^2-y^2}$ and d_{z^2} orbitals) has zero (empty, e_g^0), 2 (half-filled e_g^2) or 4 (completely filled, e_g^4) electrons, the arrangement of these electrons in this set is said to be symmetrical arrangement and e_g set of orbitals is said to be symmetrically filled. On the other hand, if e_g set has 1 or 3 electrons, this arrangement of electrons is said to be asymmetrical arrangement of electrons and e_g set is said to be a symmetrically filled. Thus:

- (i) e_g^0 (empty), e_g^2 (half-filled), e_g^4 (completely filled) ... symmetrically filled orbitals
- (ii) e_g^1, e_g^3, \dots asymmetrically-filled orbitals.

Note: We know that d^3 ion is represented by the configuration, $t_{2g}^3 e_g^0$ in LS octahedral complexes. In this configuration, both the electrons of e_g set are assumed to be present in d_{z^2} orbital and the $d_{x^2-y^2}$ orbital remains vacant. Thus $t_{2g}^3 e_g^2$ configuration is represented as $t_{2g}^3 d_{z^2}^2 d_{x^2-y^2}^0$. In this configuration, although e_g set is half-filled, it is said to asymmetrically filled, since both the electrons are in d_{z^2} orbital.

7.12.2.2 Jahn-Teller Theorem or Jahn-Teller Effect

In 1937, Jahn and Teller put forward a remarkable theorem to explain why some six coordinated complexes (octahedral complexes) undergo distortion and have distorted octahedral geometry. **This theorem states that if a molecule / complex possessing any shape (excepting linear shape) has an unsymmetrically filled set of degenerate orbitals is unstable and hence undergoes distortion. This distortion takes place**

in such a way that the symmetry and energy of the molecule / complex is lowered and hence the molecule / complex becomes more stable. This theorem does not say which type of distortion will occur in the molecule / complex. Thus, according to this theorem, if the electrons in d -orbitals of the central metal ion of a regular octahedral complex are asymmetrically arranged, the octahedral shape of the complex will get distorted, since the electrons present in a symmetrically-filled d -orbitals will repel some ligands to greater extent while other ligands will be repelled to lesser extent. The distortion in geometry of non-linear system due to Jahn-Teller effect is called Jahn-Teller distortion.

7.12.3 DISTORTION SHOWN BY OCTAHEDRAL COMPLEXES OF dx IONS ($x = 0$ TO 10)

Octahedral complexes of some d^x ions show strong distortion while some ions show weak distortion. There are also some ions which do not show any distortion.

1. **d^0 ion ($t_{2g}^0 e_g^0$ with $n = 0$):** Octahedral complexes of d^0 ion do not show any distortion. Examples of such complexes are $[\text{TiX}_6]^{2-}$ where $X = \text{F, Cl}$.
2. **d^1 ion. Ti^{3+} ion is a d^1 ion:** This ion is present in octahedral complex ion, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. In the ground state d^1 configuration is represented as $t_{2g}^1 e_g^0$, t_{2g}^1 electron may be present in d_{xy} orbital d_{xz} / d_{yz} orbital. When t_{2g}^1 electron is present in d_{xy} orbital, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion undergoes strong distortion and assumes compressed distorted octahedral geometry. On the other hand, if t_{2g}^1 electron is present in d_{xz} or d_{yz} orbital, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ undergoes strong distortion and assumes elongated distorted octahedral geometry.
3. **d^2 ion:** E.C. of d^2 ion is $t_{2g}^2 e_g^0$ ($n = 2$). This configuration has asymmetrically filled t_{2g} orbitals and empty e_g orbitals. Hence octahedral complexes of d^2 ion show slight distortion.
4. **d^3 ion:** E.C. of d^3 ion is $t_{2g}^3 e_g^0$ ($n = 3$). In this configuration t_{2g} orbitals are symmetrically filled and e_g orbitals are empty. Octahedral complexes of d^3 ion, therefore, do not show any distortion (no distortion). Examples of such complexes are $[\text{Cr}(\text{ox})_3]^{2-}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ etc.
5. **(a) d^4 (HS) ion:** Cr^{2+} and Mn^{3+} ions are d^4 ions. Since the configuration of weak field (HS) 6-coordinated complexes of these ions viz $t_{2g}^3 e_g^1$ has asymmetrically-filled e_g set, these complexes show strong distortion in their octahedral shape. One electron present in e_g set may be present either in d_{z^2} orbital or in $d_{x^2-y^2}$ orbital. If the single electron is supposed to be present in $d_{x^2-y^2}$ orbital, this electron is repelled by four ligands lying on $+x$, $-x$ and $+y$ and $-y$ axes. On the other hand, if the single electron is assumed to be present in orbital, this electron is repelled by two ligands lying on $+z$ and $-z$ axes. Thus the energy of $d_{x^2-y^2}$ orbital increases relative to d_{z^2} orbital. This leaves $d_{x^2-y^2}$ orbital empty. Thus the configuration of d^4 ion in high spin octahedral complexes is $(t_{2g})^3 (d_{z^2})^1 (d_{x^2-y^2})^0$ and not $(t_{2g})^3 (d_{z^2})^0 (d_{x^2-y^2})^1$. The repulsion between the single

electron present in d_{z^2} orbital and the two ligands along $+z$ and $-z$ axes (trans or axial ligands) results in the elongation of the two axial ligands. Thus the octahedral complex assumes elongated distorted octahedral structure in which two trans metal-ligand bonds are long and four metal-ligand bonds in xy square plane are short. In the formation of elongated distorted octahedral structure both t_{2g} and e_g sets present in octahedral complex split. The splitting of t_{2g} and e_g sets in various d -orbitals takes place in the way as shown at (c) of Fig. 7.43. This configuration shows that d_{z^2} orbital has lower energy than $d_{x^2-y^2}$ orbital and hence has one electron. The energy difference between d_{xy} and d_{yz}, d_{zx} pair is very small and hence each of these orbitals also has one electron only. Example of elongated distorted octahedral complexes containing d^4 ion are CaF_2 and MnF_3 crystals and $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Mg}(\text{C}_2\text{O}_4)_3]^{3-}$ ion. CrF_2 crystal has distorted rutile (TiO_2) structure in which Cr^{2+} ion is octahedrally surrounded by six F^- ions (ligands). The length of four $\text{Cr}^{2+} - \text{F}$ bonds in xy plane is 2.0\AA each and that of the two $\text{Cr}^{2+} - \text{F}$ bonds along z -axis is 2.43\AA . Thus the crystal of CrF_2 has elongated distorted octahedral structure. Fig. 7.43 shows that the distribution of d^4 electrons in the splitted d -orbitals is as $d_{yz}^1 d_{zx}^1 d_{xy}^1 d_{z^2}^1 d_{x^2-y^2}^0$.

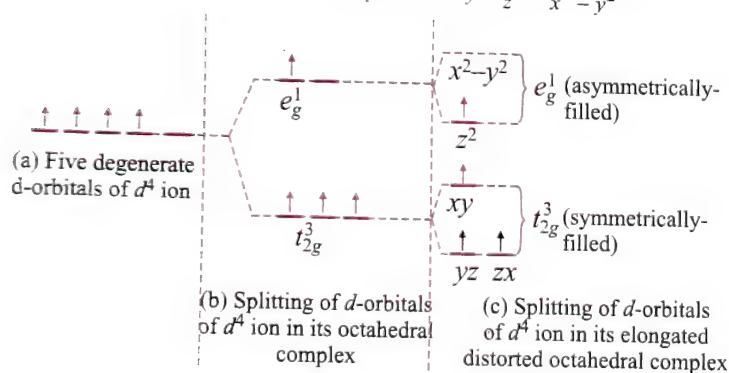


Fig. 7.43 Distribution of d^4 electrons in octahedral and tetragonally elongated distorted octahedral complexes of d^4 ion.

(b) $d^4(\text{LS})$ ion: E.C. of d^4 ion in LS state is $t_{2g}^4 e_g^0$ which contains asymmetrically filled t_{2g} orbitals and empty e_g orbitals. LS octahedral complexes of d^4 ion, therefore, show slight distortion.

6. (a) $d^5(\text{HS})$ ion (e.g. Mn^{2+} , Fe^{2+} etc.): E.C. of d^5 ion in HS state is $t_{2g}^3 e_g^2$ ($n = 5$). This configuration shows that t_{2g} and e_g orbitals both are symmetrically filled. Hence HS octahedral complexes of d^5 ion do not undergo any distortion. Examples of such complexes are $[\text{MnF}_6]^{4-}$, $[\text{FeF}_6]^{3-}$ etc.

(b) $d^5(\text{LS})$ ion: E.C. of d^5 ion in LS state is $t_{2g}^5 e_g^0$ ($n = 1$). This configuration has asymmetrically filled t_{2g} orbitals and empty e_g orbitals. Hence LS octahedral complexes of d^5 ion undergo slight distortion.

7. (a) $d^6(\text{HS})$ ion (e.g. Co^{2+} ion): E.C. of d^6 ion in HS state is $t_{2g}^4 e_g^2$ ($n = 4$). This configuration has asymmetrically filled t_{2g} orbitals and symmetrically filled e_g orbitals. HS

octahedral complexes of d^6 ion, therefore, undergo slight distortion. Example of such complex is $[\text{CoF}_6]^{3-}$.

(b) $d^6(\text{LS})$ ion (e.g. Co^{3+} ion): E.C. of d^6 ion in LS states is $t_{2g}^4 e_g^0$ ($n = 0$). This configuration has symmetrically filled t_{2g} orbitals and empty e_g orbitals. Hence LS octahedral complexes of d^6 ion undergo no distortion. Example of such octahedral complex is $[\text{Co}(\text{NH}_3)_6]^{3+}$.

8. (a) $d^7(\text{HS})$ ion: E.C. of d^7 ion in HS state is $t_{2g}^5 e_g^2$ ($n = 3$). This configuration has asymmetrically filled t_{2g} orbitals and symmetrically filled e_g orbitals. HS octahedral complexes of d^7 ion, therefore, show slight distortion.

(b) $d^7(\text{LS})$ ion (e.g. Co^{2+}): E.C. of d^7 ion in LS octahedral complexes of this ion is $t_{2g}^6 e_g^1$ ($n = 1$). This configuration has symmetrically filled t_{2g} orbitals and asymmetrically filled e_g orbitals, e_g^1 electrons is present in $d_{x^2-y^2}$ orbital and d_{z^2} orbital is vacant. Thus $t_{2g}^6 e_g^1 = t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^0$. Due to the presence of asymmetrically-filled e_g orbitals in $t_{2g}^6 e_g^1$ configuration, LS octahedral complexes of d^7 ion undergo large distortion. $[\text{Co}(\text{diars})_3]^{2+}$ is an example of octahedral complex which undergoes large distortion.

9. (a) d^8 ion (HS) (e.g. Ni^{2+}): E.C. of d^8 ion in HS state is $t_{2g}^6 e_g^2 = t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^1$ ($n = 2$). In this configuration t_{2g} and e_g orbitals both are symmetrically filled. Hence HS octahedral complexes of d^8 ion do not show any distortion. Examples of such complexes are $[\text{NiF}_6]^{4-}$, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ etc. Energy level diagram showing the filling of 3d orbitals with d^8 electrons is given in Fig. 7.44.

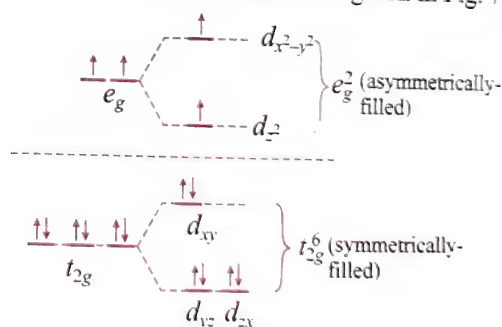


Fig. 7.44 Energy level diagram showing the filling of 3d orbitals with eight electrons of d^8 configuration in HS state

(b) $d^8(\text{LS})$ ion (e.g., Ni^{2+} , Pd^{2+} , Pt^{2+} etc.): E.C. of d^8 ion in LS state is $t_{2g}^6 e_g^2 = t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^1$ ($n = 0$). In this configuration, t_{2g} orbitals are symmetrically filled. Although e_g orbitals are half filled, these orbitals are said to be asymmetrically filled, since both the e_g electrons are present in d_{z^2} orbital. Hence LS octahedral complexes of d^8 ion show large distortion giving elongated distorted octahedral geometry. Examples of such complexes are $[\text{Mg}(\text{diars})_2\text{I}_2]^0$ where $\text{M} = \text{Ni}^{2+}$, Pd^{2+} , Pt^{2+} .

The splitting of t_{2g} (lower energy) and e_g (higher energy) orbitals in elongated distorted octahedral complexes takes place as shown in Fig. 7.45. This figure shows that the distribution of d^8 electrons in the splitted d -orbitals is as $d_{yz}^2 d_{zx}^2 d_{xy}^2 d_{z^2}^1 d_{x^2-y^2}^1$.

Since all electrons are present in the paired state, these complexes are diamagnetic. The elongation of axial bond lengths in $[\text{Ni}^{2+}(\text{diars})_2\text{I}_2]^0$ is so larger that $[\text{Ni}^{2+}(\text{diars})_2\text{I}_2]^0$ assumes square planar geometry.

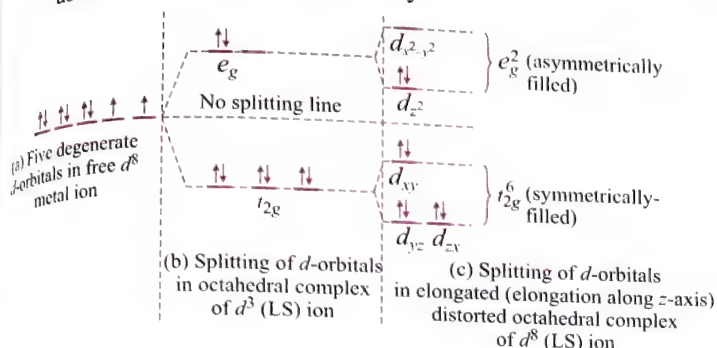


Fig. 7.45 Splitting of d -orbitals in tetragonally elongated octahedral complexes of d^8 in LS state

10. d^9 ion (e.g. Cu^{2+} ion): E.C. of d^9 ion (Cu^{2+} ion) is $t_{2g}^6 e_g^3$ ($n = 1$). In this configuration t_{2g} orbitals are symmetrically filled but both e_g orbitals are asymmetrically filled. It is due to the presence of a symmetrically filled e_g orbitals that octahedral complexes of Cu^{2+} ion undergo large distortion

and assume either elongated distorted octahedral geometry or compressed distorted octahedral geometry. If $t_{2g}^6 e_g^3$ configuration is $t_{2g}^5 d_{z^2}^1 d_{x^2-y^2}^1$, octahedral geometry assumes elongated distorted octahedral geometry. On the other hand, if $t_{2g}^6 e_g^3$ configuration is $t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^1$, the octahedral geometry assumes compressed distorted octahedral geometry.

The splitting of t_{2g} and e_g orbitals in elongated distorted octahedral and compressed distorted octahedral geometry has been discussed on the subsequent pages of this chapter.

11. d^{10} ion (e.g. Zn^{2+}). E.C. of d^{10} ion is $t_{2g}^6 e_g^4$. This configuration has t_{2g} and e_g orbitals both symmetrically filled. Hence octahedral complexes of d^{10} ion do not show distortion. Examples of such complexes are $[\text{Zn}(\text{NH}_3)_6]^{2+}$, $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ etc.

Whatever has been said above has been summarized in Table 7.21. The information given in this table can be used to find out the conditions under which the octahedral complex of a given d^x ion ($x = 0$ to 10) undergoes no distortion, slight distortion or large distortion.

Table 7.21 Summary of distortion taking place in octahedral complexes of d^x ions ($x = 0$ to 10), sym. = symmetrically filled, asym. = asymmetrically filled.

d^x ion ($x = 0$ to 10)	$t_{2g}^a e_g^b$ configuration	Nature of t_{2g} and e_g orbitals		Distortion
		t_{2g}	e_g	
d^0	$t_{2g}^0 e_g^0$	Empty	Empty	No distortion
d^1	$t_{2g}^1 e_g^0 = d_{xy}^1 d_{yz}^0 d_{xz}^0 e_g^0$	Asym	Empty	Strong distortion (Compressed distortion)
	$t_{2g}^1 e_g^0 = d_{xy}^0 d_{yz}^1 d_{xz}^0 e_g^0$ or $d_{xy}^0 d_{yz}^0 d_{xz}^1 e_g^0$	Asym	Empty	Large distortion (Elongated distortion)
d^2	$t_{2g}^2 e_g^0$	Asym	Empty	Slight distortion
d^3	$t_{2g}^3 e_g^0$	Asym	Empty	No distortion
d^4 (HS)	$t_{2g}^3 e_g^1 = t_{2g}^3 d_{z^2}^1 d_{x^2-y^2}^0$	Asym	Asym	Strong distortion (Elongated distortion)
d^4 (LS)	$t_{2g}^4 e_g^0$	Asym	Asym	Slight distortion
d^5 (HS)	$t_{2g}^3 e_g^2$	Sym	Sym	No distortion
d^5 (LS)	$t_{2g}^5 e_g^0$	Asym	Empty	Slight distortion
d^6 (HS)	$t_{2g}^4 e_g^2$	Asym	Sym	Slight distortion
d^6 (LS)	$t_{2g}^6 e_g^0$	Sym	Empty	No distortion
d^7 (HS)	$t_{2g}^5 e_g^2$	Asym	Sym	Slight distortion

d^7 (LS)	$t_{2g}^6 e_g^1 = t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^0$	Sym	Asym	Large distortion
d^8 (HS)	$t_{2g}^6 e_g^2$	Sym	Sym	No distortion
d^8 (LS)	$t_{2g}^6 e_g^2 = t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^0$	Sym	Asym	Large distortion (Elongated distortion)
d^9	$t_{2g}^6 e_g^3 = t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^1$	Sym	Asym	Large distortion (elongated distortion)
d^9	$t_{2g}^6 e_g^3 = t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^2$	Sym	Asym	Large distortion (elongated distortion)
d^{10}	$t_{2g}^6 e_g^4$	Sym	Sym	No distortion

7.12.3.1 Conditions for No Distortion

Octahedral complexes of d^x ions whose both the sets of d -orbitals viz t_{2g} and e_g are symmetrically filled ($t_{2g}^0, t_{2g}^3, t_{2g}^6$ and e_g^0, e_g^2, e_g^4) undergo no distortion, i.e., such complexes are perfectly octahedral in shape. Perfectly octahedral shape is because of the fact that the electrons present in symmetrically filled t_{2g} and e_g sets repel all the six ligands to the same extent. This discussion shows

that since the ions viz $d^0(t_{2g}^0 e_g^0, n=0)$, $d^3(t_{2g}^3 e_g^0, n=3)$, $d^5(t_{2g}^3 e_g^2 - \text{HS with } n=5)$, $d^6(t_{2g}^6 e_g^0 - \text{LS with } n=0)$, $d^6(t_{2g}^6 e_g^0 - \text{LS with } n=0)$, and $d^8(t_{2g}^6 e_g^2 - \text{HS with } n=2)$ ($d^{10}(t_{2g}^6 e_g^4$ with $n=0$) have t_{2g} and e_g sets symmetrically filled, octahedral complexes of these ions do not undergo distortion, i.e., these complexes are perfectly octahedral.

7.12.3.2 Conditions for Slight (Negligible) Distortion

Octahedral complexes of d^x ions whose t_{2g} set of orbitals is asymmetrically-filled ($t_{2g}^1, t_{2g}^2, t_{2g}^4, t_{2g}^5$) and e_g sets is symmetrically-filled (e_g^0, e_g^2) undergo slight distortion. Small distortion is because of the fact that since the lobes the three asymmetrically-filled orbitals of t_{2g} set do not lie directly in the path of the ligands, the electrons present in t_{2g} set of orbitals cause small distortion in octahedral complexes. Thus the octahedral complexes $d^2(t_{2g}^2 e_g^0, n=0)$, $d^4(t_{2g}^4 e_g^0 - \text{LS with } n=2)$, $d^5(t_{2g}^5 e_g^0 - \text{LS with } n=1)$, $d^5(t_{2g}^4 e_g^2 - \text{HS with } n=4)$, and $d^7(t_{2g}^5 e_g^2 - \text{HS with } n=3)$ ions undergo small distortion.

7.12.3.3 Conditions for Large Distortion

Octahedral complexes of d^x ions whose t_{2g} set is symmetrically-filled (t_{2g}^0, t_{2g}^3 and t_{2g}^6) and e_g set is asymmetrically-filled [$e_g^1(d_{z^2}^1 d_{x^2-y^2}^0)$, $e_g^3(d_{z^2}^2 d_{x^2-y^2}^1)$, $e_g^3(d_{x^2-y^2}^0 d_{z^2}^1)$ [e_g^2 set ($d_{z^2}^2 d_{x^2-y^2}^0$) is also regarded as asymmetrically-filled set in LS

octahedral complexes of d^8 ion ($d^8 = t_{2g}^6 e_g^2 = t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^0$)] undergo strong distortion and assume either tetragonally elongated distorted octahedral geometry or compressed distorted octahedral geometry.

Thus the octahedral complexes of the following d^x ions undergo strong (large) distortion.

$d^1(t_{2g}^1 e_g^0)$, $d^4(\text{HS})(t_{2g}^3 d_{z^2}^1 d_{x^2-y^2}^0 - \text{elongated distortion})$,

$d^7(\text{LS})(t_{2g}^6 e_g^1 = t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^0)$,

$d^8(\text{LS})(t_{2g}^6 e_g^2 = t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^0 - \text{elongated distortion})$,

$d^9(t_{2g}^6 e_g^3 = t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^1 - \text{elongated distortion})$,

$d^9(t_{2g}^6 e_g^3 = t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^2 - \text{compressed distortion})$.

Cause of large (strong) distortion: Since the lobes of both orbitals of e_g set (d_{z^2} and $d_{x^2-y^2}$ orbitals) lie directly in the path of the six ligands (six ligands of an octahedral complex lie on the three axes), the electrons present in this set, if arranged asymmetrically i.e., if e_g set contains 1 or 3 electrons, repel some ligands to greater extent and repel other ligands to lesser extent. This ligand repulsion causes large distortion in octahedral shape of 6-coordinated complexes.

7.12.3.4 Splitting of t_{2g} and e_g Orbitals in Elongated Distorted Octahedral Complexes of Cu^{2+} Ion

The splitting of t_{2g} and e_g sets of orbitals into various d -orbitals has been shown in Fig. 7.46

In order to explain the splitting pattern shown in Fig. 7.46, we start with the splitting of d -orbitals in t_{2g} and e_g sets in octahedral complexes. We know that in the splitting of d -orbitals in octahedral complexes, the energy of t_{2g} set (i.e. d_{xy} , d_{yz} and d_{zx} orbitals) is decreased and that of e_g set (i.e., d_{z^2} and $d_{x^2-y^2}$ orbitals) is increased. Now in elongated distorted octahedral complexes, since metal-ligand bond distance along z -axis is longer, d -orbitals having z component (i.e., d_{yz} , d_{zx} and d_{z^2} orbitals) experience less repulsion from the ligands than they do in octahedral complex

while the d -orbitals in xy plane (i.e., d_{xy} and $d_{x^2-y^2}$ orbitals) experience more repulsion than they do in octahedral complex. Consequently the energy of d_{yz} , d_{zx} and d_{z^2} orbitals decreases while that d_{xy} and $d_{x^2-y^2}$ orbitals increases. Note that d_{yz} and d_{zx} orbitals still remain degenerate as they are in octahedral complex. Above discussion shows that the order of energy of the splitted-orbitals in tetragonally elongated octahedral complex becomes as:

$$(d_{yz} = d_{zx}) < d_{xy} < d_{z^2} < d_{x^2-y^2} \quad (\text{Also see Fig. 7.46})$$

The relative order of energy of various orbitals shown above indicates that in the elongated distorted octahedral complexes the distribution of $3d^9$ electrons ($t_{2g}^6 e_g^3$) of Cu^{2+} ion is as shown in Fig. 7.46. This figure shows that the arrangement of d^9 electrons in various d -orbitals can be written as:

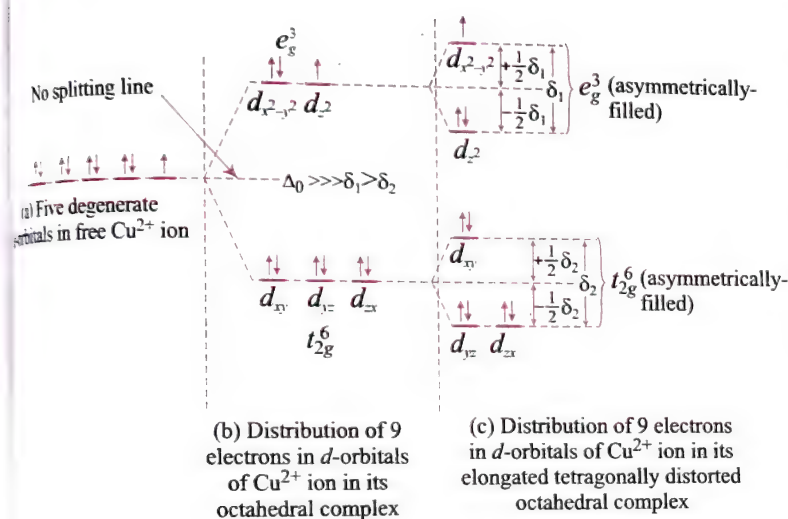
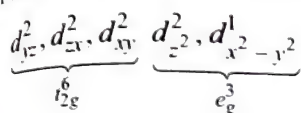
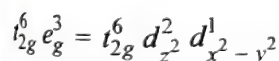


Fig. 7.46 Distribution of 9 electrons of Cu^{2+} ion ($\text{Cu}^{2+} = 3d^9$) in the splitted d -orbitals in its tetragonally elongated distorted octahedral complexes.

Thus the configuration, $t_{2g}^6 e_g^3$ can be written as:

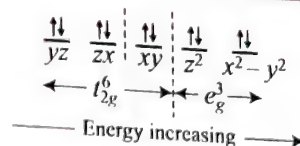


This configuration shows that tetragonally elongated octahedral complexes have two electrons in d_{z^2} orbital and one electron in $d_{x^2-y^2}$ orbital, since d_{z^2} orbital has lower energy than $d_{x^2-y^2}$ orbital.

7.12.3.5 Elongated Distortion in Octahedral Geometry of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ Complexes

Tetrammine copper (II) complex, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is actually $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ in which the two axial H_2O ligands are at larger distances (along the z -axis) from the central Cu^{2+} ion than the four equatorial NH_3 ligands are of shorter distances (along x - and y -axes). Thus this complex has two long (axial) and four short (equatorial) bonds. Consequently the complex, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ has tetragonally elongated distorted octahedral geometry.

The distribution of d^9 electrons of Cu^{2+} ion in five d -orbitals is as:



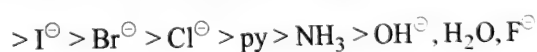
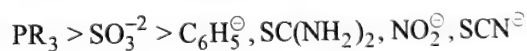
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion also has tetragonally elongated distorted octahedral geometry. The tetragonally elongated geometry (distorted octahedral geometry) of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions is due to the asymmetric arrangement of three electrons in e_g orbitals. This arrangement contains two electrons in d_{z^2} orbital and one electron in $d_{x^2-y^2}$ orbitals, since d_{z^2} orbital has lower energy than $d_{x^2-y^2}$ orbital. The effect of the asymmetric arrangement of three electrons in e_g orbitals on the octahedral geometry of the complex ions is called Jahn-Teller effect.

7.13 TRANS EFFECT

Trans effect is the labilization (making more reactive) of ligands that are trans to certain other ligands, which can thus be regarded as trans, directing ligands. It is attributed to electronic effects and it is most notable in square planar complexes, although it can also be observed for octahedral complexes. The cis effect is most often observed in octahedral transition metal complexes.

In addition to this **kinetic trans effect**, trans ligands also have an influence on the ground state of the molecule, the most notable ones being bond length and stability the term **trans influence** is sometimes used to distinguish it from **kinetic effect** however more specific terms such as **structural trans effect** or **thermodynamic trans effect** is also used.

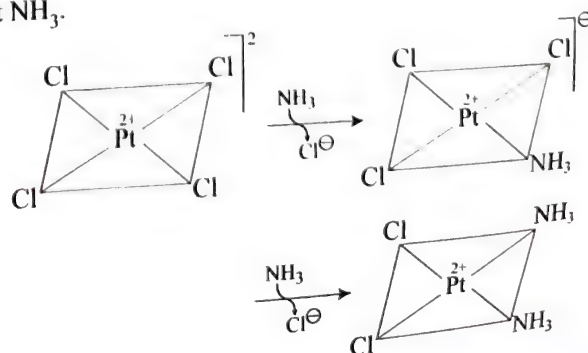
The intensity of the trans effect (as measured by the increases in rate of substitution of trans ligand) follow this sequence.



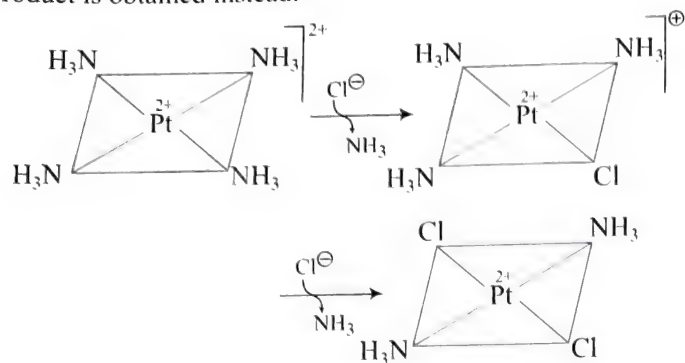
(i) $(\text{CN}^\ominus, \text{CO}$ and NO are powerful trans directions while OH^\ominus and H_2O are very poor.)

(ii) $\text{M}-\text{X}$ bond is more labile than $\text{M}-\text{N}$ bond.

Example: The classical example of the trans effect is the synthesis of **cisplatin** and its trans isomer. Starting from $[\text{PtCl}_4]^{2-}$, the first NH_3 ligand is added to any of the four equivalent position at random. However since Cl^\ominus has a greater trans effect than NH_3 , the second NH_3 is added trans to a Cl^\ominus and therefore cis to the first NH_3 .



If, on the other hand, one starts from $[\text{Pt}(\text{NH}_3)_4]^{2+}$, the trans product is obtained instead:



Explanation: The trans effect in square planar complexes can be explained in terms of an addition/elimination mechanism that goes through a trigonal bipyramidal intermediate. Ligands with a high trans effect are in general those with high π -acidity (as in case of phosphine, PH_3) or low-ligand lone pair- $d\pi$ repulsions (as in case of hydride, H^-), which prefer the more π -basic equatorial sites in the intermediate. The second equatorial position is occupied by the incoming ligand, due to the principle of microscopic reversibility, the departing ligand must also leave from an equatorial position. The third and final equatorial site is occupied by the trans ligand, so the net result is that the kinetically favoured product is the one in which the ligand trans to the one with the largest trans effect is eliminated.

Structural trans effect: The structural trans effect can be measured experimentally using x-ray crystallography, and is observed as a stretching of the bonds between the ligand and the ligand trans to a trans-influencing ligand.

Stretching by as much as 0.2\AA occurs with strong trans-influencing ligands such as hydride (H^-) ion. A cis influence can also be observed, but is smaller than the trans influence. The relative importance of cis and trans influences depends on the formal electronic configuration of metal center, and explanations have been proposed based on the involvement of the atomic orbitals.

Factors: The trans effect is used to distinguish between the cis and the trans isomers of the type $[\text{PtA}_2\text{X}_2]$ where A = amine and X = halide.

- Thiourea (tu) replaces the halides only in the trans isomer but all the four ligands are replaced in the cis-isomer.
- Trans effect is important with the large polarizable metal ions, the order of metals is: $\text{Pt}^{+2} > \text{Pd}^{+2} > \text{Ni}^{+2}$.
- The trans directors are either polarizable (I^-) or multiple bonded (CO , CN^- etc.).
- The two π -ligands, for the d -orbitals of the metal ion, will tend to labilize each other when present trans to each other, but in the cis-position they will not complete.
- The stronger π -bonding ligand will dominate and weaken the other bond.
- In $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$, the Pt—Cl bond trans to (C_2H_4) (ethylene) is larger than the cis-bond.
- Pt—Cl (trans) stretching frequency is lower than the P—Cl (cis) frequencies showing weaker Pt—Cl bonds trans to ethylene group.

Limitation

- Ammonia which cannot form π -bonds should not be destabilized by the π -bonding ligands.
- π -bonding alkenes show trans effect for halogens but not for the nitrogen ligands.
- Many ligands like hydride (H^-) or methyl are good trans directors but cannot form π -bond.

ILLUSTRATION 7.54

The correct increasing order of trans-effect of the following species is:

- $\text{CN}^- > \text{Br}^- > \text{C}_6\text{H}_5^- > \text{NH}_3$
- $\text{NH}_3 > \text{CN}^- > \text{Br}^- > \text{C}_6\text{H}_5^-$
- $\text{CN}^- > \text{C}_6\text{H}_5^- > \text{Br}^- > \text{NH}_3$
- $\text{Br}^- > \text{CN}^- > \text{NH}_3 > \text{C}_6\text{H}_5^-$

Sol. c. The intensity of trans effect depends on increase in rate of substitution of the trans ligands $\text{CN}^- > \text{CH}_3^- > \text{C}_6\text{H}_5^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3 > \text{F}^-$.

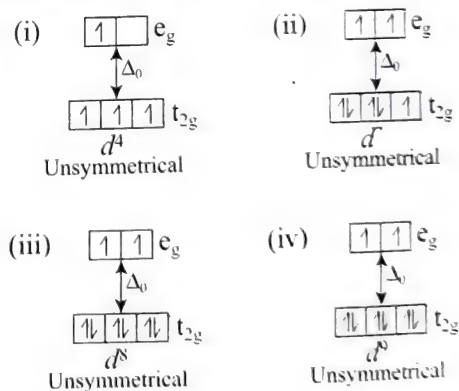
ILLUSTRATION 7.55

Jahn-Teller effect is not observed in high spin complexes of

- d^9
- d^7
- d^8
- d^4

Sol. c. Jahn Teller effect: This is geometric distortion which occurs in unsymmetrical octahedral complexes.

For example: High spin complexes of (high spin)



Jahn Teller effect is not observed in d^8 configuration.

ILLUSTRATION 7.56

Explain the following giving reasons:

- $[\text{NiCl}_4]^{2-}$ is tetrahedral and paramagnetic, whereas $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar and diamagnetic.
- $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion is more paramagnetic than $[\text{Fe}(\text{CN})_6]^{3-}$ ion.
- $\text{Ni}(\text{CO})_4$ is tetrahedral while $[\text{Ni}(\text{CN})_4]^{2-}$ ion is square planar.
- $[\text{Co}(\text{F}_6)]^{3-}$ is a high spin complex whereas $[\text{Co}(\text{CN})_6]^{3-}$ ion is a low spin complex.

a. In the complex, $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ oxidation state of Ni is +2

Electronic configuration of Ni atom

$3d^8 4s^2$

Electronic configuration of Ni^{2+} ion

$3d^8 4s^0$

Since Cl^- ion is weak field ligand, electronic configuration of Ni^{2+} in $[\text{NiCl}_4]^{2-}$ remains the same,

Ni^{2+} ion in $[\text{NiCl}_4]^{2-}$

Since Ni^{2+} in $[\text{NiCl}_4]^{2-}$ ion is sp^3 hybridised and have two unpaired electrons it is tetrahedral and paramagnetic.

Since CN^- ion is strong field ligand, electronic configuration of Ni^{2+} in $[\text{Ni}(\text{CN})_4]^{2-}$ is

Ni^{2+} in $[\text{Ni}(\text{CN})_4]^{2-}$ ion

i.e., one electron from $3d_{x^2-y^2}$ orbital gets paired with that in $3d_{z^2}$ orbital. Thus one d -orbital ($3d_{x^2-y^2}$ orbital) becomes available for dsp^2 hybridisation which gives square planar geometry with $n = 0$. Thus $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic.

b. Oxidation state of Fe in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion is +3.

Electronic configuration of Fe ($3d^6 4s^2$)

Electronic configuration of Fe^{3+} ion ($3d^5 4s^0$)

Since H_2O is weak field ligand, no pairing of electrons takes place and

Electronic configuration of Fe^{3+} in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion

i.e. there are 5 unpaired electrons, $n = 5$.

Whereas in $[\text{Fe}(\text{CN})_6]^{3-}$, oxidation state of Fe is +3.

Electronic configuration of Fe^{3+} ion ($3d^5 4s^0$)

Since CN^- ion is strong field ligand, pairing up of electrons in 3d orbitals takes place i.e.

Electronic configuration of Fe^{3+} in $[\text{Fe}(\text{CN})_6]^{3-}$ ion

i.e. there is only one unpaired electron, $n = 1$.

Since in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion, number of unpaired electrons are more than $[\text{Fe}(\text{CN})_6]^{3-}$ ion, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is more paramagnetic than $[\text{Fe}(\text{CN})_6]^{3-}$ ion.

c. In $\text{Ni}(\text{CO})_4$, oxidation state of Ni is zero.

Electronic configuration of Ni atom ($3d^8 4s^2$)

Since CO is strong field ligands, hence pairing of electrons takes place.

Ni atom in $[\text{Ni}(\text{CO})_4]$

Because of sp^3 hybridisation, $[\text{Ni}(\text{CO})_4]$ is tetrahedral.

In $[\text{Ni}(\text{CN})_4]^{2-}$, oxidation state of Ni is +2

Ni atom

Ni^{2+} atom

Since CN^- is strong field which results in pairing up of electron present in $3d_{x^2-y^2}$ and $3d_{z^2}$ and $3d_{x^2-y^2}$ becomes available for dsp^2 hybridisation.

Ni^{2+} (in $[\text{Ni}(\text{CN})_4]^{2-}$ ion)

d. $[\text{CoF}_6]^{3-}$ is a high spin complex whereas $[\text{Co}(\text{CN})_6]^{3-}$ is a low spin complex. This can be explained as:

Co atom ($3d^7 4s^2$)

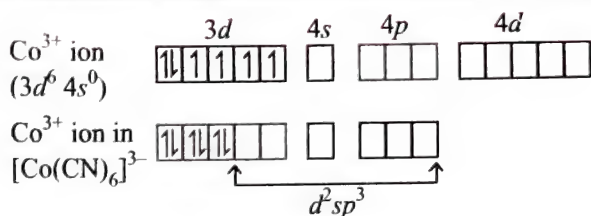
Co^{3+} ion ($3d^6 4s^0$) ($n = 4$)

Co^{3+} ion (in $[\text{CoF}_6]^{3-}$)

Since F^- ion is weak field ligand, no pairing up of electrons present in 3d orbital takes place. Since there are four unpaired electrons, $[\text{CoF}_6]^{3-}$ is paramagnetic complex. Since outer d orbitals (i.e. 4d) are involved, it is also known as high spin or outer orbital complex.

Note: Oxalate generally behaves as a weak field ligand but with Co, it behaves as a strong field ligand like NH_3 and H_2O .

In $[\text{Co}(\text{CN})_6]^{3-}$, oxidation state of Co is +3.

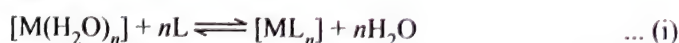


Since CN[⊖] is a strong field ligands, pairing of 3d electrons takes place, $n = 0$. Since inner d orbitals (3d) are involved in hybridisation (d^2sp^3), it is also known as low spin or inner orbital complex.

In [CoF₆]³⁻, $n = 4$ whereas in [Co(CN)₆]³⁻, $n = 0$ hence [CoF₆]³⁻ is a high spin complex whereas [Co(CN)₆]³⁻ is a low spin complex.

7.14 STABILITY OF COORDINATION COMPOUNDS IN SOLUTIONS

For the reaction,

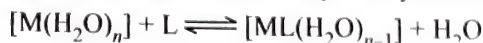


The stability of the coordination compound [ML_n] is measured in terms of the overall stability constant (equilibrium constant) given by the expression.

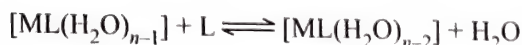
$$\beta_n = [ML_n] / [M(H_2O)_n] [L]^n$$

The above reaction, takes place in steps.

A coordination compound is formed in solution by the stepwise addition of ligands to a metal ion. Thus formation of the complex, ML_n may be supposed to take place by the consecutive n steps.

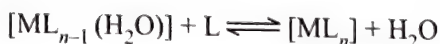


$$K_1 = \frac{[ML(H_2O)_{n-1}]}{[M(H_2O)_n][L]}$$



$$K_2 = \frac{[ML(H_2O)_{n-2}]}{[ML(H_2O)_{n-1}][L]}$$

⋮
⋮
⋮



$$K_n = \frac{[ML_n]}{[ML_{n-1}(H_2O)][L]}$$



$$\beta_n = K_1 \times K_2 \times K_3 \cdots K_n = \frac{[ML_n]}{[M(H_2O)_n][L]^n}$$

By convention, the water, H₂O displaced is ignored, as its concentration remains essentially constant.

K_1, K_2, \dots, K_n are called stepwise stability constant. In general, the values of successive stability constants decrease regularly from K_1 to K_n . β_n is called the overall stability constant (and $1/\beta_n$ is called as instability constant). The higher the overall stability constant value of the complex, the more stable it is. Alternatively, values called instability constant explain the dissociation of the complex into metal ion and ligands in the solution.

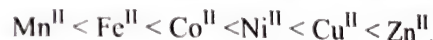
β_n , the overall stability constant is related to thermodynamic stability when the system has reached equilibrium. Stability constants of few complexes in solution are given in the following table.

System	Stability constant K
$Cu^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	4.5×10^{11}
$Cu^{2+} + 4CN^- \rightleftharpoons [Cu(CN)_4]^{2-}$	2.0×10^{27}
$Ag^+ + 4NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.6×10^7
$Co^{3+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	5.0×10^{33}

From the above values it is seen that CN[⊖] is a stronger ligand than NH₃.

Important generalisations derived from the vast data on stability constants are as follows:

- For a given metal and ligand the stability is generally greater, the greater the charge on the metal ion. Thus, stability of coordination entities of ions of charge 3+ is greater than the entities of 2 ions. Further, for the divalent ions of the first row transition elements, irrespective of the ligand involved, the stabilities vary in the **Irving-Williams Order**:



- The metal ions, '**class a**' acceptors like metals of groups 1 and 2, the inner transition elements and the early members of the transition series (groups 3 to 6) form their most stable coordination entities with ligands containing N, O or F donor atoms.
- The metal ions, '**class b**' acceptors like the transition elements—Rh, Pd, Ag, Ir, Au and Hg having relatively full d orbitals form their most stable complexes with ligands whose donor atoms are the heavier members of the N, O and F groups.
- The stability also depends on the formation of chelate rings. If L is an unidentate ligand and L-L, a didentate ligand and if the donor atoms of L and L-L are the same element, then L-L will replace L. The stabilisation due to chelation is called the **chelate effect**. It is of great importance in biological systems and analytical chemistry. The chelate effect is maximum for the 5- and 6-membered rings. In general, rings provide greater stability to the complex.
- If a multidentate ligand happens to be cyclic and there are no unfavourable steric effects, a further increase in stability occurs. This is termed the **macrocyclic effect**.

7.15 COLOUR IN COORDINATION COMPOUNDS

Coordination compounds of transition metal have fascinating colours. The study of the colour of transition metal complexes can be divided into two categories:

a. Colour of the complex ions whose central metal atom contains partially filled d -orbitals.

When white light which is composed of many different colours falls on a coloured complex ion or complex compound of a transition metal, the ion or complex absorbs some portion of the white light and the remaining portion of the incident light is transmitted or reflected by the complex/ion. The colour of absorbed light and transmitted are different from each other. The colour of the transmitted light is called complimentary colour of the adsorbed light, given in Table 7.22. The complimentary colour is the colour generated from the wavelength left over.

Table 7.22 Colour of absorbed and transmitted radiations

Colour of the absorbed light/radiation	Range of the wavelength (Å) of the absorbed light	Colour of the transmitted light (complimentary colour of the absorbed light)
Violet	4000 – 4500	Yellow green
Blue	4500 – 4800	Yellow
Green blue	4800 – 4900	Orange
Blue green	4900 – 5000	Red
Green	5000 – 5600	Violet (almost purple)
Yellow green	5600 – 5750	Violet
Yellow	5750 – 5900	Blue
Orange	5900 – 6250	Green blue
Red	6250 – 7500	Blue green

For example:

- Hydrated Cu^{2+} ion, i.e. $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ absorbs yellow radiation and transmits blue radiation and hence looks blue to our eyes.
- Hydrated Ti^{3+} ion, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorbs green radiation hence transmits the radiation of purple colour. Hydrated Ti^{3+} ion, therefore looks violet (almost purple).
- Anhydrous Co^{3+} compounds absorb the radiation of red colour and therefore appear blue green. Whereas, hydrated Co^{2+} ion i.e. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion absorbs blue green radiation and therefore appears red.

Colours of some common hexahydrated transition metal complex ions $[\text{M}(\text{H}_2\text{O})_6]^{n+}$ are given in Table 7.23.

Table 7.23 Colours of some common $[\text{M}(\text{H}_2\text{O})_6]^{n+}$ ions

Ions	Electronic configuration	Colour of the ion violet
Ti^{3+}	$3d^1 (n = 1)$	Violet (almost purple)
V^{3+}	$3d^2 (n = 2)$	Green
V^{2+} , Cr^{3+}	$3d^3 (n = 3)$	Violet

Cr^{2+}	$3d^4 (n = 4)$	Blue
Mn^{3+}	$3d^4 (n = 4)$	Violet
Mn^{2+}	$3d^5 (n = 5)$	Pink
Fe^{3+}	$3d^5 (n = 5)$	Yellow
Fe^{2+}	$3d^6 (n = 4)$	Green
Co^{2+}	$3d^7 (n = 3)$	Pink (red)
Ni^{2+}	$3d^8 (n = 2)$	Blue green
Cu^{2+}	$3d^9 (n = 1)$	Blue

Colours of transition metal ions in aqueous solution corresponds to their aqua complexes.

Following table gives the wavelength of light adsorbed and the coloured observed in some coordination entities.

Table 7.24 Relationship between the wavelength of light absorbed and the colour observed in some coordination entities

Coordination entities	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue green	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow orange
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet	Pale yellow
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600	Red	Blue
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498	Blue green	Purple

The colour of the absorbed light also depends on the nature of the ligands. For example, Ni^{2+} ion in $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ absorbs red and hence has blue green colour. Ni^{2+} ion in $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ion absorbs yellow colour and is therefore blue in colour. Thus, although the central metal ion is same in both the complex ions, these ions absorb radiation of different colours and therefore have different colours.

Energy associated with the wavelength of the radiation absorbed can be calculated as follows.

Let $[\text{M}(\text{H}_2\text{O})_6]^{n+}$ ion absorbs the radiation of wavelength $\lambda \text{ Å}$. Then the frequency or wave number (in cm^{-1}) corresponding to this wavelength is given by

Frequency ν or wave number (in cm^{-1}) of the absorbed radiation of wave length of $\lambda \text{ Å}$.

$$= \frac{1}{\lambda \text{ (in Å)}} = \frac{1}{\lambda \times 10^{-8} \text{ cm}}$$

$$= \frac{10^8}{\lambda} \quad (\because 1 \text{ Å} = 10^{-8} \text{ cm})$$

This frequency is associated with energy whose magnitude can be calculated in kcal mol^{-1} or kJ mol^{-1} by using the fact that

$$350 \text{ cm}^{-1} = 1 \text{ kcal mol}^{-1}$$

$$\text{and } 83.7 \text{ cm}^{-1} = 1 \text{ kJ mol}^{-1}$$

$$1 \text{ kcal mol}^{-1} = \frac{?}{\text{cm}^{-1}}$$

The above conversion is obtained by using the following relation:

$$E = N_A h c \bar{\nu}, \quad \bar{\nu} = \frac{E}{N_A h c}$$

where

$$\begin{aligned} E &= 1 \text{ kcal mol}^{-1} \\ N_A &= 6.02 \times 10^{23} \text{ mol}^{-1} \\ h &= 6.6 \times 10^{-34} \text{ Js} \end{aligned}$$

OR

$$h = \frac{6.6 \times 10^{-34} \times 10^{-3}}{4.18} \text{ kcal}$$

$$c = 3 \times 10^8 \text{ ms}^{-1} = 3 \times 10^8 \times 10^2 \text{ cm s}^{-1}$$

$$\bar{\nu} = \frac{1 \text{ kcal mol}^{-1} \times 4.18}{6.02 \times 10^{23} \text{ mol}^{-1} \times 6.6 \times 10^{-34} \times 10^{-3} \text{ kcal} \times 3 \times 10^8 \times 10^2 \text{ cm s}^{-1}} = 350 \text{ cm}^{-1}$$

Therefore, 1 kcal mol⁻¹ = 350 cm⁻¹

$$1 \text{ kJ mol}^{-1} = \frac{?}{\text{cm}^{-1}}$$

The above conversion is obtained as follows:

$$E = N_A h c \bar{\nu} \quad \bar{\nu} = \frac{E}{N_A h c}$$

where $E = 1 \text{ kJ mol}^{-1}$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$h = 6.6 \times 10^{-34} \text{ Js} = 6.6 \times 10^{-34} \times 10^{-3} \text{ kJs}$$

$$c = 3 \times 10^8 \text{ ms}^{-1} = 3 \times 10^8 \times 10^2 \text{ cms}^{-1}$$

$$\begin{aligned} \bar{\nu} &= \frac{1 \text{ kJ mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1} \times 6.6 \times 10^{-34} \times 10^{-3} \text{ kJs} \times 3 \times 10^8 \times 10^2 \text{ cms}^{-1}} \\ &= 83.7 \text{ cm}^{-1} \end{aligned}$$

Therefore, 1 kJ mol⁻¹ = 83.7 cm⁻¹

Thus, since $350 \text{ cm}^{-1} = 1 \text{ kcal mol}^{-1}$

$$\frac{10^8}{\lambda} \text{ cm}^{-1} = \frac{10^8}{350 \times \lambda (\text{in } \text{\AA})} \text{ kcal mol}^{-1} \quad \dots (i)$$

Equation (i) shows that

Energy associated with a wavelength of $\lambda \text{ \AA}$

$$= \frac{10^8}{350 \times \lambda (\text{in } \text{\AA})} \text{ kcal mol}^{-1} \quad \dots (ii)$$

Similarly, since $83.7 \text{ cm}^{-1} = 1 \text{ kJ mol}^{-1}$

$$\frac{10^8}{\lambda} \text{ cm}^{-1} = \frac{10^8}{83.7 \times \lambda (\text{in } \text{\AA})} \text{ kJ mol}^{-1} \quad \dots (iii)$$

Equation (iii) shows that

Energy associated with a wavelength of $\lambda \text{ \AA}$

$$= \frac{10^8}{83.7 \times \lambda (\text{in } \text{\AA})} \text{ kJ mol}^{-1} \quad \dots (iv)$$

Equations (ii) and (iv) both show that the energy associated with the absorbed radiation is inversely proportional to the wavelength of the radiation but directly proportional to the frequency of the radiation.

Explanation of the violet (purple) colour of octahedral [Ti(H₂O)₆]³⁺ ion by d-d electron transition.

The complex [Ti(H₂O)₆]³⁺, which is violet in colour, is an octahedral complex where the single electron (Ti³⁺ is a 3d¹ system) in the metal d orbital is in the 't_{2g}' level in the ground state of the complex. The next higher stable state available for the electron is the empty 'e_g' level. If light corresponding to the energy of yellow-green region is absorbed by the complex, it would excite the electron from 't_{2g}' level to the 'e_g' level (t_{2g}¹e_g⁰ → t_{2g}⁰e_g¹). Consequently, the complex appears violet in colour). The crystal field theory thus, attributes the colour of the coordination compounds of d-d transition of the electron.

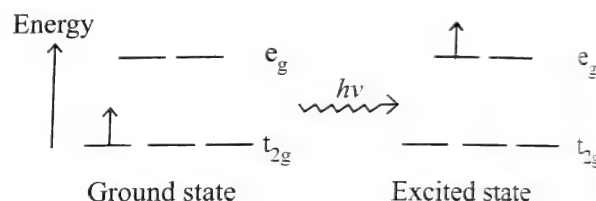


Fig. 7.47 Transition of an electron in [Ti(H₂O)₆]³⁺

b. Colour of the complex ions whose central atom contains empty or completely filled d-orbitals.

The transition metal complex ions whose central atom contains empty (d⁰ configuration) or completely filled d-orbitals (d¹⁰ configuration) are colourless. This is due to the fact that in such cases d-d transition is not possible. Thus [Sc(H₂O)₆]³⁺ (d¹ system), [Ti(H₂O)₆]⁴⁺ (d⁰ system), [Cu(H₂O)₆]²⁺, [Zn(H₂O)₆]²⁺ (d¹⁰ system) are colourless.

7.16 ORGANOMETALLIC COMPOUNDS

Organometallic compounds are the compounds which contain at least one metal carbon bond. They also include the compounds in which C-atom is bonded not only to metal atom but also to metalloids (i.e., element less EN than carbon) e.g., boron (B) silicon (Si), arsenic (As) and tellurium (Te).

However, they are not confined to this definition or to their name. Compounds like carbides, cyanides, carbonates and carbonyls, though they contain metal-carbon bonds are not considered as organometallic compounds by convention, because their properties are much different than those of other compounds belonging to the class of organometallic compounds. For example, K₂[Zn(CN)₄] and [Ni(CO)₄], are coordination compounds but not

an organometallic.

Moreover, although a compound may contain many hydrocarbon radicals, it is not classified as organometallic when its all the C-atoms are linked to metal through atoms like O, N or S as in trimethyl orthoborate, $B(OCH_3)_3$, i.e. $H_3C-O-B \begin{matrix} \nearrow OCH_3 \\ \searrow OCH_3 \end{matrix}$

Which is thus not considered as organometallic compounds since no C-atom is directly linked to boron (B).

But $CH_3B(OCH_3)_2$ is an organometallic compound since it contains at least one B—C bond i.e., $H_3C-B \begin{matrix} \nearrow OCH_3 \\ \searrow OCH_3 \end{matrix}$

Similarly $(C_3H_7O)_4Ti$ is also not an organometallic compound but $C_6H_5Ti(OC_3H_7)_3$ is because it has one Ti—C bond.

1. Likewise diethyl zinc, $(C_2H_5)_2Zn$ is an organometallic compound in which two ethyl groups are directly linked with Zn forming Zn—C bonds.

2. Organometallic compounds containing either the hydrocarbon radicals attached to the metal such as $(C_2H_5)_4Pb$ or containing hydrocarbon radicals along with H atoms attached to the metal such as $(CH_3)_3SiH$ are called **Simple organometallic compounds** whereas those containing at least one hydrocarbon radical along with some others groups attached to metal such as $R-Mg-X$ and $(C_4H_9)_2SnCl_2$ are called **mixed organometallic compounds**.

3. Organometallic compounds are not found in the nature.

7.16.1 CLASSIFICATION OF ORGANOMETALLIC COMPOUNDS

Based on the nature of M—C bond, they are broadly classified into two types as follows:

a. σ -bonded organometallic compounds of the main groups (s and p block) elements: These are covalent compounds with (M—C) σ bonds in which bonding consists of localised (M—C) σ bonds formed by sharing of an electrons pairs.

The s- and p-block organometallics are named according to the substituent names used in **organic chemistry**. For example methyl lithium for CH_3Li and trimethylboron for $B(CH_3)_3$ which is also called trimethylborane, taking it to be a derivative of its hydrogen counterpart. Thus, $Si(CH_3)_4$ [Fig. 7.48(e)] and $As(CH_3)_3$ [Fig. 7.48(f)] are tetramethylsilane and trimethylarsane respectively.

The oxidation number of the metallic element in an organometallic compound is based on the organic moiety being considered to be anionic. For example, in $Zn(CH_3)_2$ and CH_3 group is taken to be negatively charged (1^-). Thus, oxidation number of zinc is 2+. The bond in alkyls of s-block elements is highly polar ($M^{\delta+}-C^{\delta-}$) in the organometallic compounds of groups 14, 15 and 16, the M—C bonds are of relatively lower polarity. Methyl compounds of Li, Na, Be, Mg and Al are associated through alkyl bridges and

multicentre two electron bonds. The structures of some representative main group organometallic compounds are shown in Fig. 7.48.

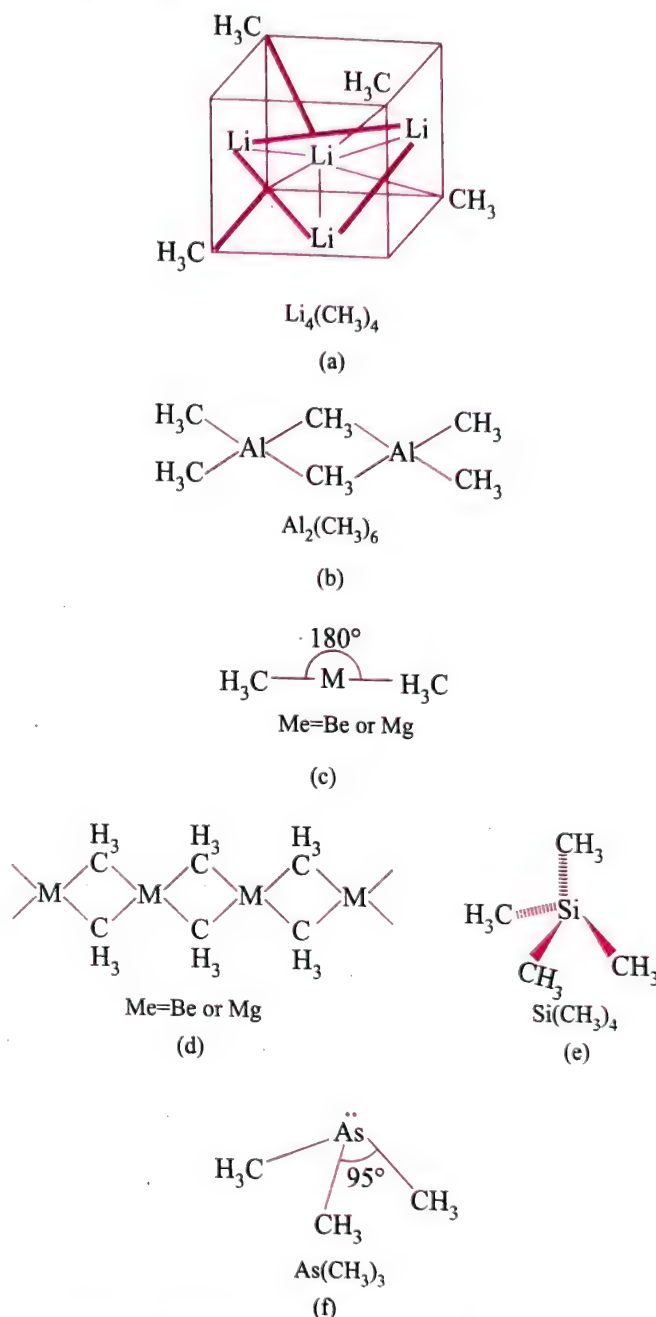


Fig. 7.48 Structures of some representative main group organometallic compounds

Their structures have been represented by empirical formulas though their actual structures are complex.

For example, $(CH_3)_2Be$ and $(CH_3)_2Mg$ have bridge structures as represented in Fig. 7.48 (c and d).

Similarly CH_3Li (methyl lithium) exists as tetramer.

Likewise, $(CH_3)_3Al$ (trimethyl aluminium) exists as a dimer in which two methyl groups acts as bridges between two Al-atoms as shown in Fig. 7.48(b).

Organometallic compounds of electropositive metals are strong reducing agents. They are pyrophoric and ignite spontaneously in air.

- b. 1. **π -bonded organometallic compounds of d and f-block elements – π complexes:** Transition metals form organometallic compounds of this type. The formation of these compounds cannot be explained in terms of simple covalent bonding.

Zeise's salt: The compound trichloridoetheneplatinate (II), $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^\ominus$ has the structure shown in Fig. 7.49.

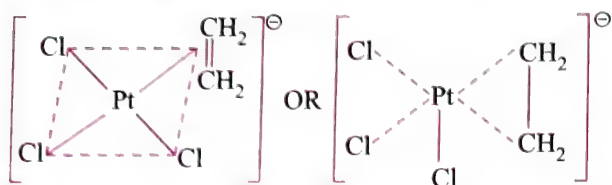


Fig. 7.49 Structures of Zeise's salt $[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]^\ominus$

EAN of Ferrocene

Number of electrons = 6

Number of electrons = 24

Number of electrons = 6

EAN = 36 electrons

EAN rule is valid

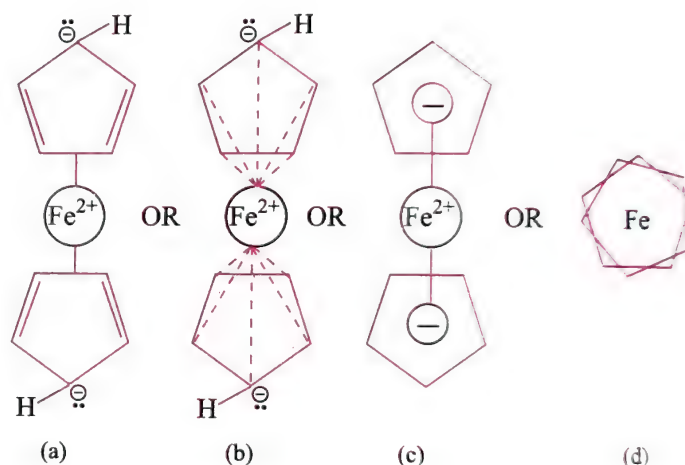


Fig. 7.50 (a-d) Structure of metallocene, Ferrocene $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ (OR) $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$

Note: η^5 represents the number of C-atoms bond to the metal, i.e. 5-C-atoms.

- ii. Ferrocene is composed of Fe^{2+} sandwiched between two cyclopentadienyl anions and held together by π -complexation. There are no (C-Fe) σ -bonds, as evidenced by the fact that the two rings freely rotate. The most stable conformation is a staggered one with the rings not flush.
- iii. Ferrocene is stable because its Fe^{2+} has a full shell of 18 electrons, six of its own (present in its five 3d atomic orbitals) and six from each cyclopentadienyl anion. It also retains the aromaticity of the each cyclopentadienyl anions.
- iv. Many transition metals form sandwich compounds with aromatic compounds providing the combined number of valence shell electrons is 18, e.g. dibenzenechromium $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ or $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$, six from Cr, and six from each benzene.

Note: In these compounds the number following η -(eta, the Greek word) represents the number of C-atoms bound to the metal in the compound.

2. Sandwich compounds (Ferrocene and dibenzene chromium).

- i. The synthesis of highly stable compound Ferrocene [bis-(cyclopentadienyl) iron(II)] or $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$ (Fig. 7.50) in 1951 was a land mark in the advancement of modern organometallic chemistry. It is called **sandwich compound**.

EAN of Dibenzene chromium

Number of electrons = 6

Number of electrons = 24

Number of electrons = 6

EAN = 36 electrons

EAN rule is valid

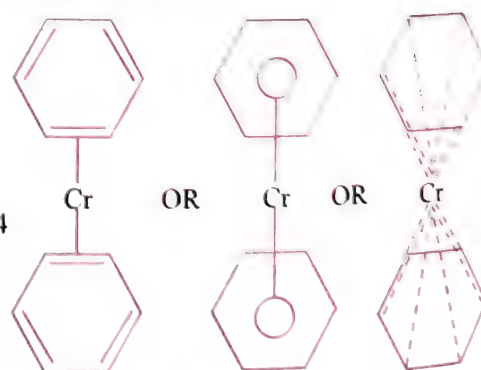


Fig. 7.51 Structure of dibenzene chromium $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$

3. **f-Block organometallic compound:** In late 1970s, the first f-block organometallic compound was prepared, e.g. $[\text{Th}^+ \text{H}^{-1} (\text{OR})^{-1} [\eta^5\text{-C}_5\text{Me}_5)_2]$ or Alkoxohydridobis

(pentamethylcyclopentadienyl) thorium (IV) (Fig. 7.52) the ligand C_5Me_5 , i.e., pentamethylcyclopentadienyl ion forms stable f-block compounds.

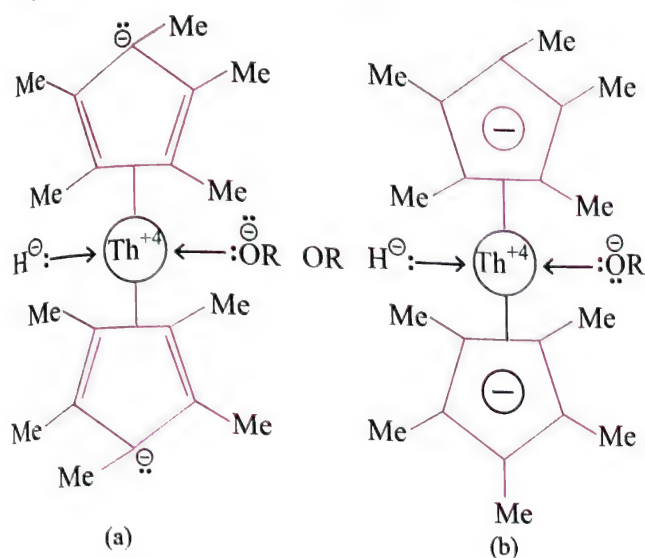


Fig. 7.52 (a-b) Structure of $[Th H (OR) (\eta^5-C_5Me_5)_2]$

7.16.2 BONDING OF ALKENES TO A TRANSITION METAL

According to Dewar, the metal to alkene bond consists of two parts:

- Overlap of the filled π -orbital of the alkene with an acceptor vacant d-orbital on the metal atom when σ -donation from filled π -orbital of alkene into vacant d-orbital on the metal occurs.
- π back donation from a filled d-orbital on the metal into vacant antibonding orbital of alkene. Thus according to this view, the metal-alkene bond involves some double bond character Fig. 7.53(a and b).

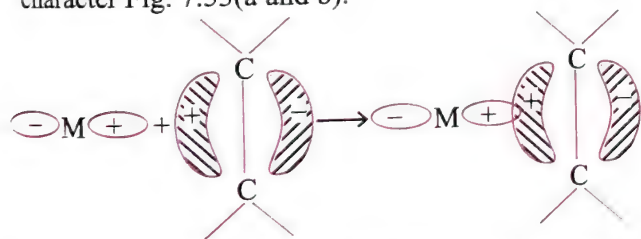


Fig. 7.53 (a) σ -donation from filled p-orbitals of the alkene into a vacant d-orbital on the metal

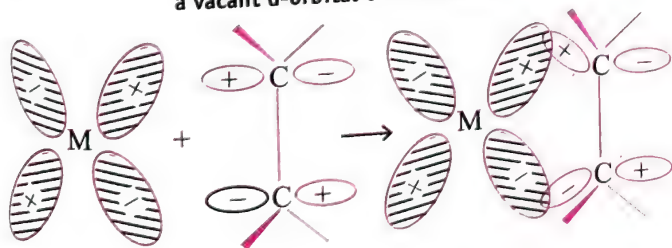


Fig. 7.53 (b) π -back donation from a filled d-orbital on the metal into the vacant antibonding orbital of alkene

7.17 METAL CARBONYLS

A widely studied and important class of organometallic compounds is that of metal carbonyls. The **homoleptic carbonyls** (compounds containing carbonyl ligands only) are formed by most of the transition metals (d metals). The metals constituting the central

part of the d block form stable, neutral binary carbonyls like:

$[V(CO)_6]$, $[Cr(CO)_6]$, $[Mo(CO)_6]$, $[W(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, $[Co_2(CO)_8]$, $[Co_4(CO)_{12}]$, $[Ni(CO)_4]$, etc. Outside the central part of d -block, the metal carbonyls are usually unstable.

7.17.1 CARBONYLS—STRUCTURE AND BONDING

Homoleptic binary metal carbonyls have simple, well-defined structures.

Tetracarbonylnickel(0) is tetrahedral, pentacarbonyliron(0) is trigonal bipyramidal while hexacarbonylchromium(0) is octahedral. Decarbonyldimanganese(0) is made up of two square pyramidal $Mn(CO)_5$ unit joined by a $Mn-Mn$ bond. Octacarbonyldicobalt(0) has a $Co-Co$ bond bridged by two CO groups (Fig. 7.54).

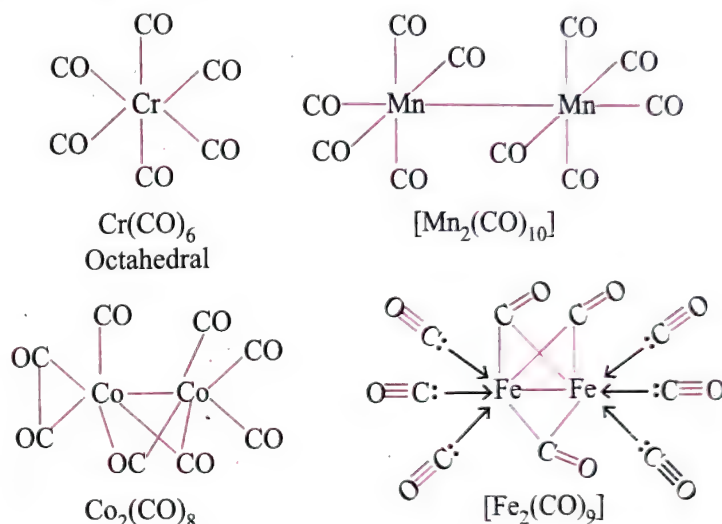


Fig. 7.54 Structure of some representative homoleptic metal

7.17.2 PROPERTIES OF METAL CARBONYLS

- Most of the metal carbonyls are solids at room temperature and atmospheric pressure. The only exceptions are nickel and iron carbonyls which are liquids.
- Mononuclear carbonyls are volatile and toxic. Further, they are either colourless or they have a light colour. For example $Fe(CO)_5$ is light-staw coloured liquids. On the other hand, polynuclear carbonyls have a deep colour. $Fe_3(CO)_{12}$, dodecacarbonyl triiron(0), for example is a deep grass green solid.
- They are soluble in hydrocarbon solvents, the only exception being $Fe_2(CO)_9$, i.e., enneacarbonyl diiron(0).
- Their reactivity is partly due to the central (metal atom and partly due to the CO ligands.

7.17.3 USES OF METAL CATALYSTS

- They are used as industrial catalysts.
- They are used as precursors in synthesis of organic compounds.

7.17.4 BONDING IN METAL CARBONYLS

The metal-carbon bonds in metal carbonyls have both σ and π character. The formation of bonds between the metal and carbon atom of carbon monoxide is described below.

The first overlap takes place between the filled bonding π_{2p} orbital of the carbon monoxide with an empty metal d-orbital resulting in a σ -bond between the metal and carbon atom of carbon monoxide. Here, donation of lone pair of electrons on carbon into a vacant d-orbital of the metal takes place. As CO is a weak base/weak donor, the σ -bond formed with the metal atom is weak.

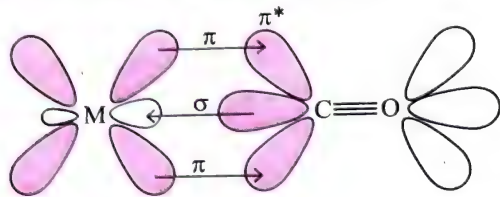


Fig. 7.55 (a) σ -overlap. Donation of lone pair of electrons on C-atom into a vacant d-orbitals on the metal, i.e. formation of (M-C) σ -bond
(b) π -overlap. Donation of electrons from a filled metal d-orbitals into a vacant antibonding π^* -orbital of CO, i.e., formation of (M-C) π bond

The second overlap takes place between the filled metal d-orbital with an empty antibonding π_{2p}^* orbital of the carbon monoxide resulting in additional π bond between the metal and same carbon monoxide molecule. Here, donation of electrons from a filled metal d-orbital into a vacant antibonding π^* -orbital of CO occurs (back bonding). Here, CO is acting as an acceptor ligand.

The effect of σ bond formation strengthens π bond and vice versa. This is called **synergic effect** (i.e., working together towards the same goal). Thus, as a result of synergic effect, the bond between CO and metal is strengthened.

Further, as explained above, a weak σ bond is formed by donation of electron pair from carbon to metal ($M \leftarrow C \equiv O$) and a stronger π bond (second bond) is formed by back donation of electrons from filled d-orbital of metal into empty antibonding π^* orbital of carbon ($\pi M \rightarrow C$ bond). The total bonding is thus $M = C = C$. Thus, bond order of C - O bond is reduced from triple bond to double bond. This is supported by the fact that C - O bond length in $C \equiv O$ is 128 Å and it increases to about 1.15 Å in many carbonyls.

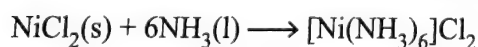
Ligands such as CO which are capable of accepting an appreciable amount of electron density from the metal atom into empty π or π^* orbital of their own are called π -acceptor or π -acid ligands.

7.18 PREPARATION OF COORDINATION COMPOUNDS

Coordination compounds are prepared by the following general methods of preparation:

1. Direct combination of reactants: Under suitable conditions, the reactants are made to react in requisite molecular proportion to produce coordination compounds. For example,

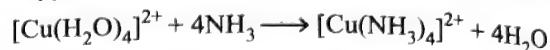
i. Metal amines can be obtained by the direct reaction between a metal salt and liquid ammonia.



ii. Reaction between ethylenediamine (en) and $PtCl_2$ gives $[Pt(en)_2]Cl_2$.

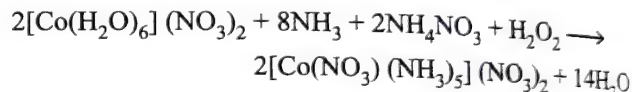


2. Substitution reactions: Most of the coordination compounds are prepared by this method. In this method stronger ligands replace the weaker ligands. For example, $[Cu(NH_3)_4]^{2+}$ complex ion is prepared by heating aqueous copper sulphate solution with ammonia.

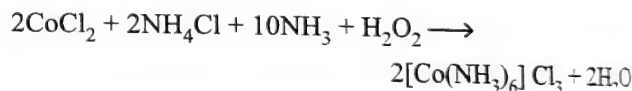


In this case, NH_3 molecules replace the water molecules (weaker ligands) surrounding the Cu^{2+} ion.

3. Redox reactions: By this method, a complex with the metal atom in a higher oxidation state than in the starting material is obtained by carrying out the process of complex formation in the presence of an oxidising agent e.g. H_2O_2 or perchlorates. For example pentaamminatocobalt (III) nitrate $[Co(NO_3)(NH_3)_5](NO_3)_2$ is prepared by adding concentrated solution of ammonia containing NH_4NO_3 to cobalt (II) nitrate solution in the presence of H_2O_2 .

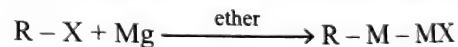
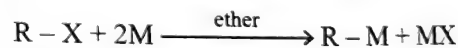


Similarly, hexaamminecobalt (III) chloride can be prepared by adding ammonium chloride to the aqueous solution of cobalt chloride made alkaline with ammonia in the presence of H_2O_2 .



a. Preparation of σ -bonded organometallic compounds:

i. **Organoalkali compounds and Grignard reagents:** These are obtained directly by the reaction between an alkyl halide and metal e.g.,

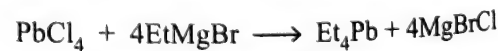


(M = Li, Na, K, X = Cl, Br, I)

ii. **Tetraalkyl tin and tetraalkyl lead:** These are obtained by reaction of metal halide with organometallic compound.



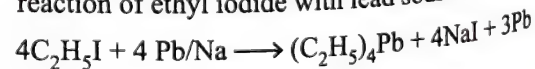
Butyl lithium Tetraethyl tin



Ethyl mag bromide Tetraethyl

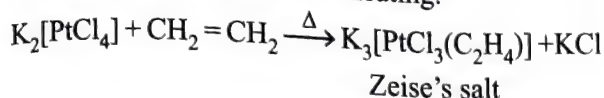
(G.R.) lead (TEL)

Tetraethyl lead (TEL) which is an important anti-knocking agent is prepared commercially by reaction of ethyl iodide with lead sodium alloy.

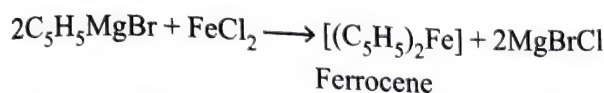


Preparation of π -complexes:

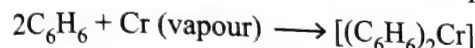
- i. **Preparation of Zeise's salt:** It is obtained by direct replacement of the weaker Cl^\ominus ligand of $[\text{PtCl}_4]^{2-}$ complex ion by ethylene on heating.



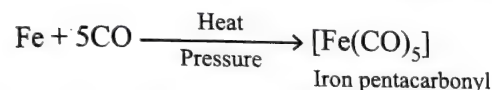
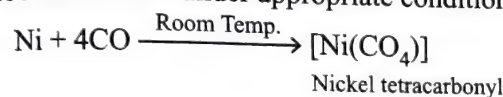
- ii. **Preparation of ferrocene:** It is obtained by the following reaction:



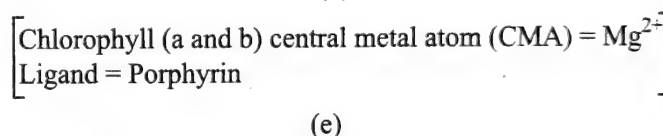
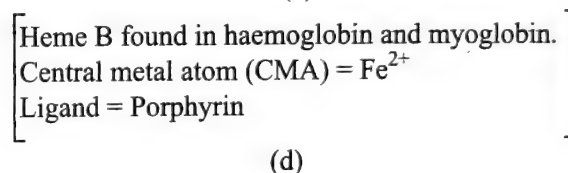
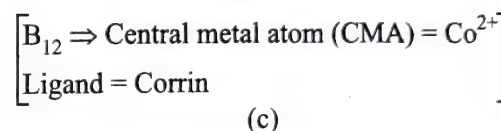
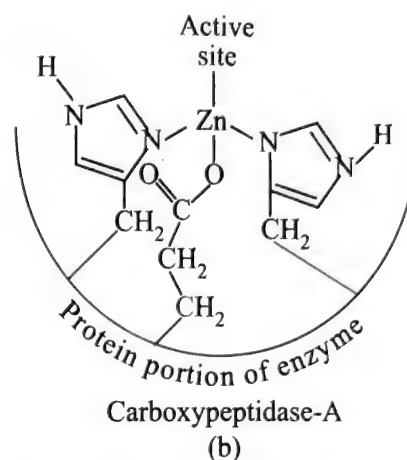
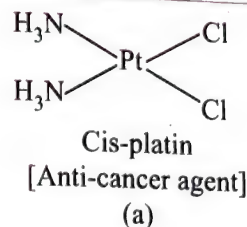
- iii. **Preparation of dibenzene chromium:** It is obtained by heating benzene with chromium vapours:



- c. **Preparation of metal carbonyls:** Metal carbonyls are obtained by direct reaction between the metal and carbon monoxide under appropriate condition e.g.,



The reaction between nickel and carbon monoxide to form volatile compounds which decomposes easily to give back nickel is used for the purification of nickel. The method is known as **Mond's process**.

**Structures of some important compounds****2. In analytical chemistry:**

- a. **In qualitative analysis:** In salt analysis, the presence of a number of basic radicals is confirmed by converting them into suitable complexes which are coloured. For example

- i. Fe^{2+} and Fe^{3+} ions are tested and distinguished by potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ and potassium ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$ as shown below:

	Reagent	Fe^{2+}	Fe^{3+}
i.	$[\text{Fe}^{2+}(\text{CN})_6]^{4-}$ Ferrocyanide ion	$\text{Fe}_2^{2+}[\text{Fe}^{2+}(\text{CN})_6]^{4-}$ Ferro-ferro cyanide (white ppt)	$\text{Fe}_4^{3+}[\text{Fe}^{2+}(\text{CN})_6]_3^{4-}$ Ferri-ferro cyanide (Prussian blue)
ii.	$[\text{Fe}^{3+}(\text{CN})_6]^{3-}$ Ferricyanide ion	$\text{Fe}_3^{2+}[\text{Fe}^{3+}(\text{CN})_6]_2^{3-}$ Ferro-ferricyanide (Turnbull's blue)	$\text{Fe}^{3+}[\text{Fe}^{3+}(\text{CN})_6]^{3-}$ Ferri-ferricyanide (Brown solution)

Note: However, Prussian blue and Turnbull's blue are chemically identical. They are mainly a mixture of ferric potassium ferrocyanide, $\text{Fe}^{\text{III}}\text{K}[\text{Fe}^{\text{II}}(\text{CN})_6]$ and ferrous potassium ferricyanide, $\text{Fe}^{\text{II}}\text{K}[\text{Fe}^{\text{III}}(\text{CN})_6]$ with some ferric ferrocyanide, $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ and ferroferricyanide, $\text{Fe}_3^{\text{II}}\text{K}[\text{Fe}^{\text{III}}(\text{CN})_6]_2$. Fe^{3+} ion partially oxidises $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ forming some $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$. Thus $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ is formed.

19 IMPORTANCE AND APPLICATIONS OF COORDINATION COMPOUNDS/COMPLEXES

The importance of coordination compounds in various fields is discussed below:

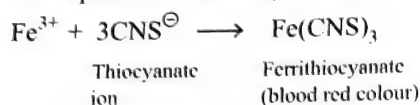
1. In biological systems:

- a. Coordination compounds are of great importance in biological systems. Familiar examples being:
- Chlorophylls** (the green pigments in plants, central to photosynthesis).
 - Haemoglobin** (the red pigment of blood, which acts as oxygen carrier) along with myoglobin (which stores oxygen and is a regulator of respiration).
 - Vitamin B_{12} cyanocobalamin, the anti-pernicious anaemia factor.

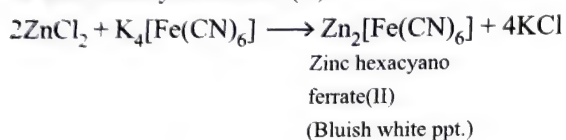
All of these, respectively, are the coordination compounds of magnesium, iron and cobalt with the macrocyclic porphyrin and corrin ligands.

- b. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, **carboxypeptidase A** and **carbonic anhydrase** (catalysts of biological system) (Figure).

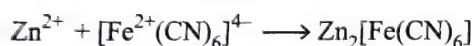
- ii. Fe^{3+} ions are also detected by adding thiocyanate ions (from ammonium thiocyanate) when a blood red colouration is obtained due to the formation of a complex i.e. ferrithiocyanate.



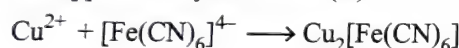
- iii. Zn^{2+} ions are tested by adding potassium ferrocyanide solution to the acidified salt solution when a **bluish white precipitate** is obtained due to formation of a complex i.e., zinc ferrocyanide or zinc hexacyanoferrate (II).



OR

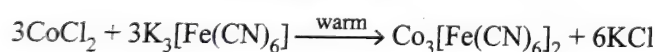


- iv. Cu^{2+} ions are tested by adding potassium ferrocyanide solution to the acidified salt solution when a chocolate colour precipitate is obtained due to formation of a complex i.e., copper ferrocyanide or copper hexacyanoferrate (II).



Chocolate colour precipitate

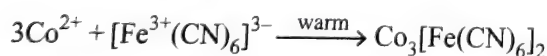
- v. a. The presence of Co^{2+} ion is tested by potassium ferricyanide test when a reddish brown precipitate is obtained due to the formation of an insoluble complex.



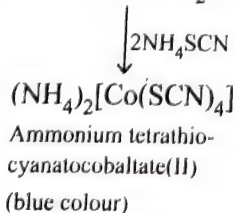
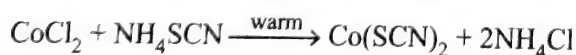
Potassium ferricyanide

Cobalt hexacyano ferrate (III)
(reddish brown ppt.)

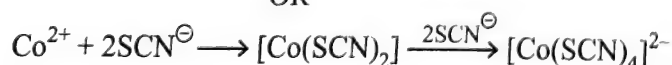
OR



- b. Co^{2+} ions are also tested by adding ammonium thiocyanate solution when a blue colour is obtained due to formation of a complex.



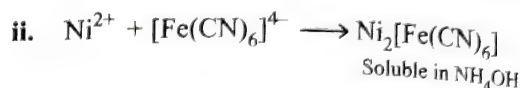
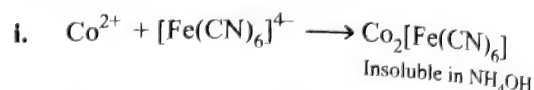
OR



- vi. **Separation of mixture of two ions:** A mixture of two ions can be separated also. Some reagent under

the same conditions, one of the metal ions may form a soluble complex while the other may form as insoluble complex.

For example, with ammonium or potassium ferrocyanide solution, Co^{2+} ion forms an insoluble complex while Ni^{2+} ion forms similar complex but soluble in NH_4OH .



3. Colour of metal ions with chelating ligands: There are many examples of the use of coordination compounds in qualitative and quantitative chemical analysis. The familiar colour reaction given by metal ions with a number of ligands (especially the chelating ligands as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Most of these reactions are highly specific and sensitive under controlled experimental conditions. Often the detection/estimation limits tend to parts per million (ppm), or even parts per billion (ppb) levels.

Familiar examples of such reagents are as follows:

dimethylglyoxime, α -nitroso- β -naphthol, 8-hydroxyquinoline, 1, 10-phenanthroline (ph), benzoic oxime (i.e. cupron), as given in following Table 7.25.

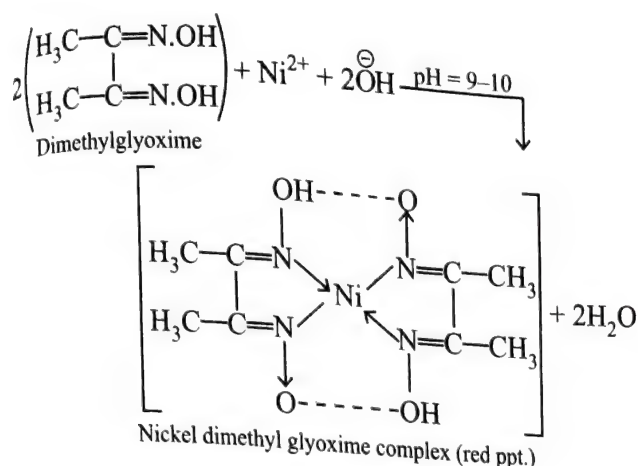
Table 7.25 Colour of metal ions with chelating (organic) reagents

	Metal ion to be estimated	Colour	pH	Organic or chelating reagents used
i.	Ni^{2+}	Red	9–10	Dimethylglyoxime
ii.	Co^{2+}	Red precipitate	–	α -Nitroso- β -naphthol
iii.	Al^{3+}	Blue	–	8-hydroxyquinoline (oxine)
iv.	Fe^{3+}	Brown	–	1, 10-Phenanthroline (ph)
v.	Cu^{2+}	Red	9–10	Benzoic oxime (i.e., cupron)

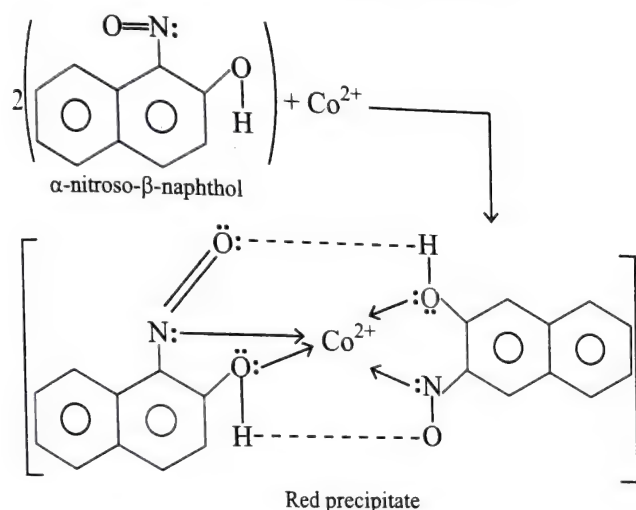
Note: In ammonical buffer, oxine (8-hydroxyquinoline) forms yellow precipitate with Mg^{2+} ion.

- i. **Ni^{2+} ions:** The presence of Ni^{2+} ion is detected by adding dimethyl glyoxime in the presence of NH_4OH (at pH =

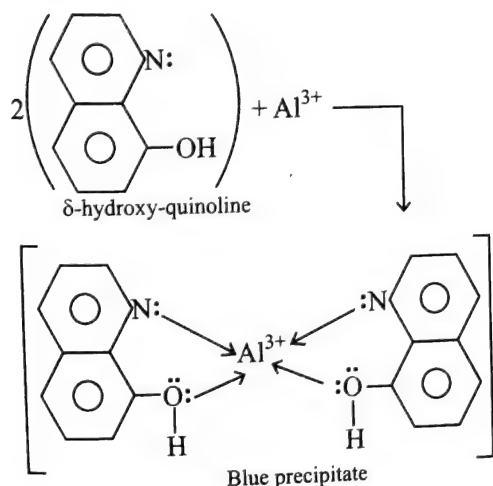
9-10) to the salt solution, a red ppt. is formed, due to formation of a complex.



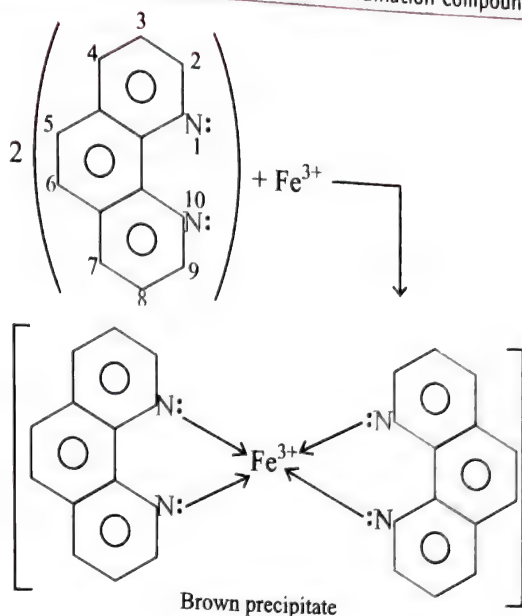
- ii. The presence of Co^{2+} ion is detected by adding α -nitroso- β -naphthol to the salt solution, a red ppt. is formed due to the formation of a complex.



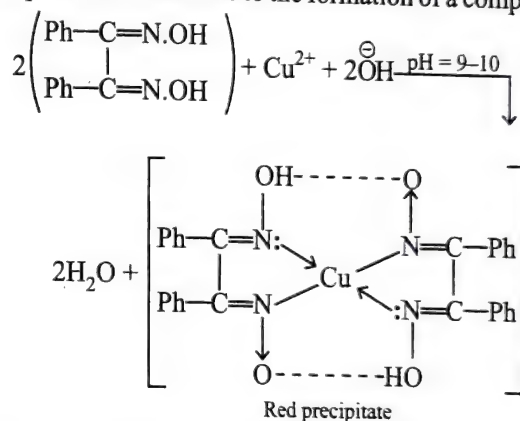
- iii. Al^{3+} : The presence of Al^{3+} ion is detected by adding 8-hydroxyquinoline to the salt solution, a blue precipitate is formed due to the formation of a complex.



- iv. Fe^{3+} : The presence of Fe^{3+} ion is detected by adding 1, 10-phenanthroline (ph) to the salt solution, a brown precipitate is formed due to the formation of a complex.

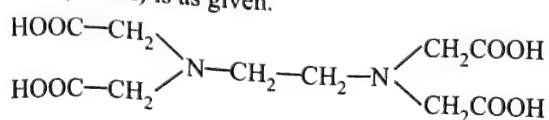


- v. The presence of Cu^{2+} ion is detected by adding benzoin oxime (also called as cuperon) in the presence of NH_4OH (at pH = 9-10) to the salt solution, a red precipitate is formed due to the formation of a complex.



4. In quantitative analysis (estimations):

- Gravimetric analysis:** The amount of metal present in a given sample can be estimated by converting a known amount of the sample into an insoluble complex which can be filtered, dried and weighed. For example, the amount of nickel present in a salt is estimated by precipitating it as nickel dimethyl glyoxime complex.
- Volumetric analysis (complexometric titrations):** A number of metal ions react completely with polydentate ligands at an appropriate pH to form complexes. Hence, the solutions of metal ions can be titrated against the solutions of the polydentate ligands in the presence of a buffer ($\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$) at pH = 10 and the end point can be detected by using a suitable indicator (eriochrome black-T). The colour must be wine red at this stage. The colour at the end point is blue. The most common polydentate ligand used is ethylene diamine tetraacetic acid (EDTA) is as given.



It is a hexadentate ligand and it coordinates through two N-atoms and four O-atoms of the —COOH groups. It is usually represented by H_4Y . Its disodium salt is commonly used because of its better solubility in water. Its formula is represented as Na_2H_2Y . It ionises as

$$Na_2H_2Y \longrightarrow 2Na^{\oplus} + H_2Y^{2-}$$

The reactions of the metal ions like Ca^{2+} , Mg^{2+} , Zn^{2+} ions etc. (in general, M^{2+}) with EDTA may be represented as follows:

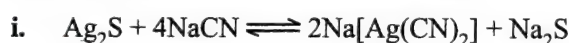


The indicators most commonly used are organic dyes such as Eriochrome black-T or Calcon.

The hardness of water due to presence of Ca^{2+} and Mg^{2+} ions is estimated by these complexometric titration.

iii. In metallurgy (extraction of metals): The noble metals like silver (Ag) and gold (Au) are extracted from their ores through the formation of cyanide complexes $[Ag(CN)_2]^{\ominus}$ $[Au(CN)_2]^{\ominus}$ respectively.

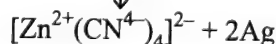
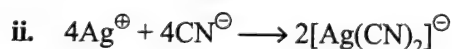
a. Extraction of silver (Ag): Silver is extracted from its ore by first dissolving the ore in NaCN solution and then precipitating out silver by adding more reactive electropositive metal, zinc (Zn).



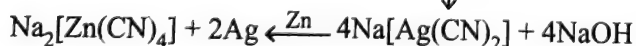
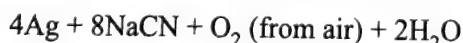
Sodium dicyano
argentate (I)



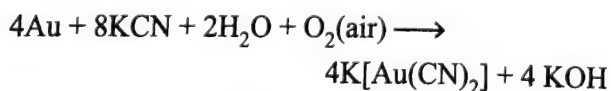
OR



iii. Native silver (Ag) also dissolve in NaCN solution in the presence of O_2 in air. Silver is precipitated by addition of scrap zinc (Zn).



b. Extraction of gold (Au): The cyanide process used for the extraction of gold is based upon the fact that gold dissolves in KCN solution in the presence of atmospheric oxygen to form a soluble cyanide complex



From the complex cyanide solution, gold is precipitated out by adding zinc scraps.

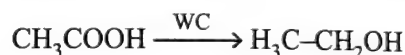
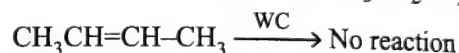
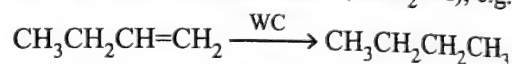


6. In purification of metals: Some metals are purified by formation of their metal carbonyls followed by their decomposition, e.g., impure nickel is converted into nickel tetracarbonyl $Ni(CO)_4$ which on decomposition gives pure nickel. This method is known as **Mond's process**.

7. In industry:

a. As catalysts: Coordination compounds are used as catalysts for many industrial processes. A few examples are given below:

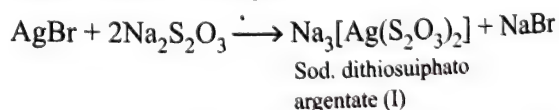
i. Homogeneous catalysis: Wilkinson catalysts, with the formula, $[RhCl(Ph_3P)_3]$, i.e., chloridotris (triphenyl) rhodium (I), is used for selective hydrogenation of alkene. The double bond at the end of the chain is hydrogenated but the double bonds elsewhere in the chain are not affected. Moreover, Wilkinson catalyst (WC) also reduces carboxylic acids ($RCOOH$) to alcohols (RCH_2OH), e.g.,



ii. Heterogeneous catalysis: Ziegler-Natta catalyst is used as heterogeneous catalysts, e.g., triethylaluminium $[(C_2H_5)_3Al]$ and titanium tetrachloride ($TiCl_4$). It is used as a catalyst for the low temperature polymerisation of alkene i.e., for the synthesis of HDPE (high density polyethylene) from ethene.

b. In electroplating: Articles can be electroplated with silver or gold much more smoothly and evenly from solutions of the complexes $[Ag(CN)_2]^{\ominus}$ and $[Au(CN)_2]^{\ominus}$ than from the solutions of simple metal ions.

c. In photography: The developed film is fixed by washing with hypo solution which dissolves the undecomposed $AgBr$ to form a complex.



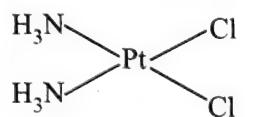
d. As dyes or pigments: Phthalocyanine blue which is an extremely stable complex of copper (II) is one of the many complex compounds used as dyes or pigments.

8. In medical field: The well-known examples are given below:

i. British anti-Lewisite (BAL) in which the chelating agent is $HSCH_2CH(SH)CH_2OH$ was developed during war time as an antidote to an arsenic containing poisonous

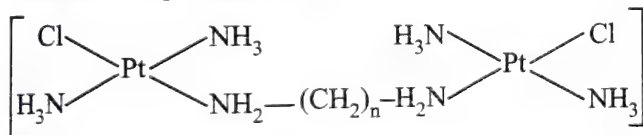
gas (Lewsite). BAL is now used to treat poisoning by As, Hg, Au, Bi, Sb and even Pb and Cd.

- ii. Calcium salt of EDTA is quite often used for treatment of lead poisoning and dermatitis and poisoning by Cr or Ni.
- iii. Metals present in toxic proportions in animals and plants are removed by **chelate therapy**, e.g., excess of copper and iron are removed by using chelating ligands, D-penicillamine and desferrioxime-B.
- iv. Recently, the platinum complex, *cis* [Pt(NH₃)₂Cl₂], known as **cisplatin** has been found to be useful in the treatment of cancer (tumours). Its structure is as follows:



cis-platin
[Anti-cancer agent]

This compound has the ability to block the uncontrolled division of cancerous cells that results in the growth of tumours. Recent studies show that *cis*-platin can cause serious side effect, including severe kidney damage. Therefore now-a-days *cis*-platin has been replaced by the following compound.



trans-isomer ($n = 2$ to 6)

- v. A number of organoarsenic compounds are used as main remedy for syphilis.
- vi. The modern surgery makes use of silicon rubbers for spare parts in the body.
- vii. Silicon rubbers are also used as cosmetic surgery.
9. **In agriculture:** To prevent infection of young plants, the seeds are treated with organometallic compounds such as ethyl mercury iodide (C₂H₅HgI).
10. **Organic synthesis:** They are widely used in the synthesis of various types of organic compounds, e.g., organolithium and organomagnesium compounds (Grignard reagent) are commonly used for the synthesis of different types of organic compounds.
11. **Future applications:** It is expected that the organometallic compounds will find an important role in the production of semiconductors for the electronic industry, pharmaceuticals, flavours and fragrances.

CONCEPT APPLICATIONS EXERCISE 7.3

1. Find out the total number of compound(s) which is/are diamagnetic in nature according to CFT.
 - I. Na₃[Cr(OX)₃]
 - II. Na₃[Co(CN)₆]
 - III. Ca[NiBr₄]
 - IV. Cl₂O

V. ClO₂

VI. ClO₃

VII. Cl₂O₇

2. Calculate total C.F.S.E. in term of Dq for the complex [MnCl₆]³⁻ and [FeBr₆]⁴⁻
3. If x = C.F.S.E. value of light pink coloured compound formed when KMnO₄ is reduced by acidified H₂S.
 y = C.F.S.E. value of light-pink coloured compound (A) formed is the reaction.



Then calculate the value of $(x - y)$.

4. C.F.S.E. for [Co(H₂O)₆]²⁺ is 6400 cm⁻¹, pairing energy for Co²⁺ is 20,000 cm⁻¹, then calculate the value of $\frac{Z_0}{10^3}$ in cm⁻¹.
5. If x = number of π -bonds in ferrocene
 y = Number of π -bonds in zeise's salt
 z = Number of π -bonds in dibenzene chromium.
Then $(x + y) - z$ is:
6. Calculate the total number of σ , π and δ -bond in the complex anion [Re₂Br₈]²⁻

Solved Examples

EXAMPLE 7.1

Three compounds A, B and C have empirical formula CrCl₃·6H₂O. When 1 g of A was kept in a container with dehydrating agent, it lost water content and attained constant weight of 0.865 g. When 1 g of B was kept in that vessel, it attained a constant weight of 0.932 g. Compound C showed no loss in water content.

- a. Find the composition of A, B and C.
- b. If an excess of aqueous AgNO₃ solution is added to 1g solution of A, B and C, what amount of AgCl will be precipitated in each case.

Sol.

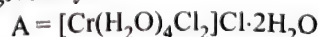
- a. Molecular mass of CrCl₃·6H₂O

$$= 52 + 35.5 \times 3 + 6 \times 18 = 266.5 \text{ g}$$

1 g of A gives $(1 - 0.865) \text{ g} = 0.135 \text{ g}$ of H₂O on dehydration

$$\therefore 266.5 \text{ g of A gives } = 0.135 \times 266.5 \text{ g} \approx 36.0 \text{ g of H}_2\text{O}$$

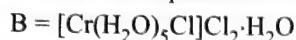
This weight of 36 g shows that on dehydration A gives two moles of H₂O (molecular mass of H₂O) = $1 \times 2 + 16 = 18 \text{ g}$, i.e., two moles of H₂O are present outside the coordination sphere in the composition of A. Thus the composition of A is given by



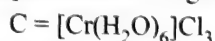
On similar grounds it can be shown that:

266.5 g of B will give $(1 - 0.932) \times 266.5$
or 18.122 g of H₂O.

This weight (=18.122 g) corresponds to one mole of H_2O . Thus B has one H_2O mole outside the coordination sphere and hence the composition of B is given by



Since C shows no loss in water content, no H_2O molecule is outside the coordination sphere, i.e., all the six H_2O molecules are inside the coordination sphere and hence the composition of C is given by



- b. Molecular mass of $\text{AgCl} = 108 + 35.5 = 143.5 \text{ g}$

Since A, i.e., $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ on treatment with AgNO_3 solution, gives one AgCl mole,

$\therefore 266.5 \text{ g}$ of A gives 143.5 g of AgCl

$\therefore 1 \text{ g}$ of A gives $\frac{143.5}{266.5} \text{ g} = 0.53 \text{ g}$ of AgCl

Since B, i.e., $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ gives two moles of AgCl .

266.5 g of B gives $2 \times 143.5 \text{ g}$ of AgCl

$\therefore 1 \text{ g}$ of B gives $\frac{2 \times 143.5}{266.5} \text{ g} = 1.076 \text{ g}$ of AgCl

Since C, i.e., $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ gives three moles of AgCl .

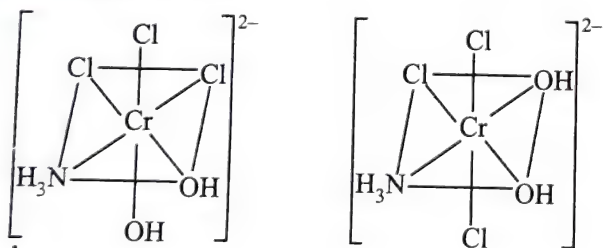
266.5 g C gives $3 \times 143.5 \text{ g}$ of AgCl .

$\therefore 1 \text{ g}$ of C gives $\frac{3 \times 143.5}{266.5} \text{ g} = 1.614 \text{ g}$ of AgCl

EXAMPLE 7.2

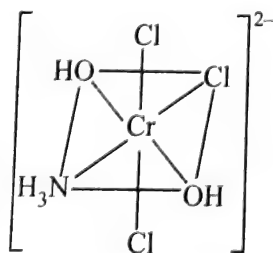
How many isomers are possible for the complex ion $[\text{Cr}(\text{NH}_3)(\text{OH})_2\text{Cl}_3]^{2-}$?

Sol. It is an example of $(\text{Ma}_3\text{b}_2\text{c})^{n\pm}$ type and 3 isomers are possible as shown below:



$\text{Cl}-\text{Cl} \Rightarrow \text{cis}$
 $\text{Cl}-\text{OH} \Rightarrow \text{cis}$
 $\text{OH}-\text{OH} \Rightarrow \text{cis}$
 $\text{Cl}-\text{NH}_3 \Rightarrow \text{cis and trans}$
 $\text{NH}_3-\text{OH} \Rightarrow \text{cis}$ (I)

$\text{Cl}-\text{Cl} \Rightarrow \text{cis and trans}$
 $\text{Cl}-\text{OH} \Rightarrow \text{cis and trans}$
 $\text{OH}-\text{OH} \Rightarrow \text{cis}$
 $\text{NH}_3-\text{OH} \Rightarrow \text{cis and trans}$ (II)



$\text{Cl}-\text{Cl} \Rightarrow \text{cis and trans}$
 $\text{Cl}-\text{OH} \Rightarrow \text{cis}$
 $\text{OH}-\text{OH} \Rightarrow \text{trans}$
 $\text{NH}_3-\text{OH} \Rightarrow \text{cis}$ (III)

EXAMPLE 7.3

For the square planar complex

$[\text{Pt}(\text{NH}_3)_4(\text{NH}_2\text{OH})\text{py}(\text{NO}_2)]^{\oplus}$, how many geometrical isomers are possible?

Sol. It is an example of $[\text{Mabcd}]^{n\pm}$ type. Three geometrical isomers are possible for the above compound.

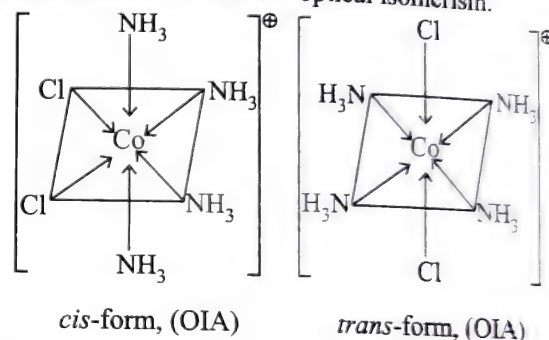
EXAMPLE 7.4

Give the total number of geometrical and optical isomers given by:

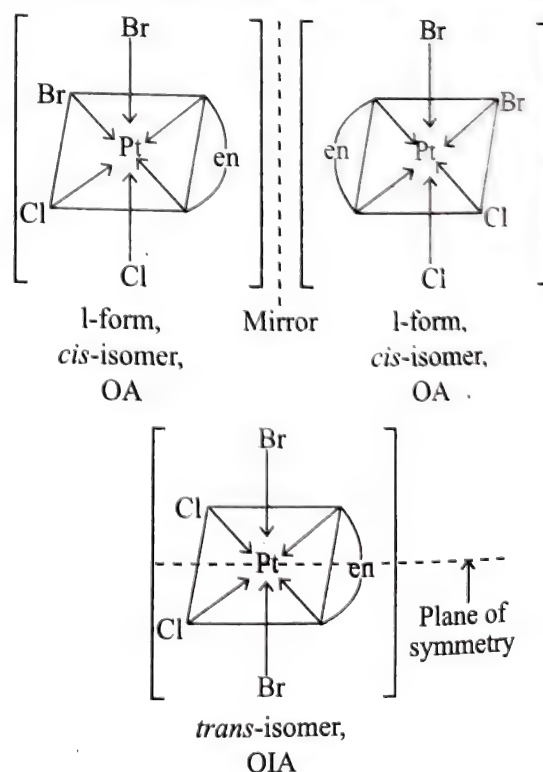
- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{\oplus}$
- $[\text{Pt}(\text{en})\text{Br}_2\text{Cl}_2]$
- $[\text{CrCl}_3(\text{H}_2\text{O})_3]$

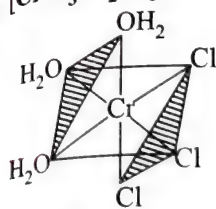
Sol.

- i. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{\oplus}$: This ion is an octahedral complex ion of $[\text{Ma}_4\text{b}_2]$ type and hence has *cis* and *trans* isomers (two geometrical isomers). Both these isomers are optically inactive and hence do not show optical isomerism.

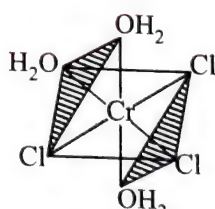


- ii. $[\text{Pt}(\text{en})\text{Br}_2\text{Cl}_2]$: This complex is an octahedral complex of $[\text{M}(\text{AA})_2\text{a}_2\text{b}_2]$ type and has *cis* and *trans*, i.e. two geometrical isomers possible. *cis*-isomer is optically active, and gives two optically active isomers (*d*- and *l*-forms) whereas *trans* form is optically inactive. Thus there are three isomers.



iii. $[\text{CrCl}_3(\text{H}_2\text{O})_3]$:


cis-form
facial (fac-)
OIA



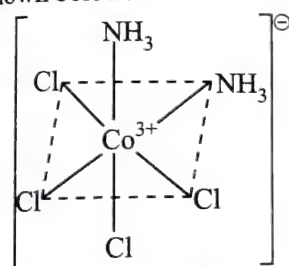
trans-form
Meridional (mer-)
OIA

EXAMPLE 7.5

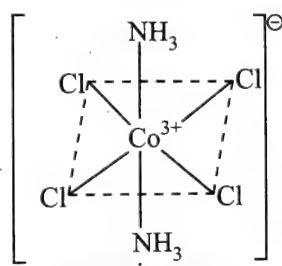
How many geometrical isomers are there for:

- $[\text{Co}(\text{NH}_3)_2\text{Cl}_4]^\ominus$
- $[\text{AuCl}_2\text{Br}_2]^\ominus$ (square planar)
- $[\text{CuCl}_2\text{Br}_2]^{2-}$ (tetrahedral)

Sol. Since $[\text{Co}(\text{NH}_3)_2\text{Cl}_4]^\ominus$ is a $[\text{Ma}_2\text{b}_4]$ type octahedral complex ion, it has two geometrical isomers which are *cis* and *trans* as shown below:

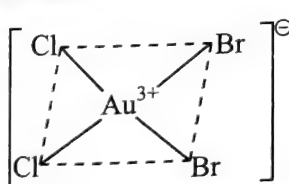


cis-isomer
(Two NH_3 ligands have
cis position)

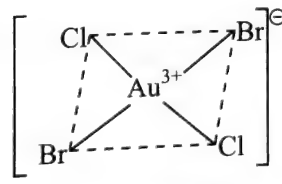


trans-isomer
(Two NH_3 ligands have
trans position)

b. Since $[\text{AuCl}_2\text{Br}_2]^\ominus$ ion is a $[\text{Ma}_2\text{b}_2]$ type square planar complex ion, it has two geometrical isomers viz. *cis* and *trans* isomers.



cis-isomer



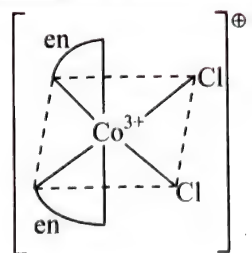
trans-isomer

c. $[\text{CuCl}_2\text{Br}_2]^{2-}$ is tetrahedral and hence has no geometrical isomer.

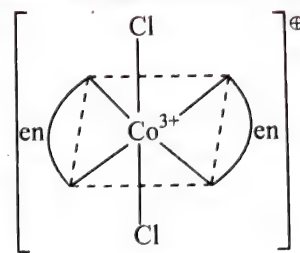
EXAMPLE 7.6

A complex of the type $[\text{M}(\text{AA})_2\text{X}_2]$ is known to be optically active. What does this indicate about the structure of the complex? Give one example of such complex.

Sol. In $[\text{M}(\text{AA})_2\text{X}_2]$ since AA is a bidentate (symmetrical) ligand and X is a monodentate ligand, CN of M (central metal atom) is 6 and hence $[\text{M}(\text{AA})_2\text{X}_2]$ has octahedral geometry. $[\text{Co}(\text{en})_2\text{Cl}_2]^\oplus$ is an example of the above type complex. This ion has *cis* and *trans* isomers (geometrical isomers). Since *cis*-isomer is optically active, it has *d*- and *l*-isomers. Since *trans*-isomer is optically inactive, it has *d*- and *l*-isomers. Since *trans* is meso form.

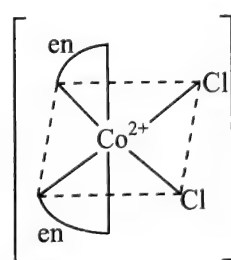


cis-isomer

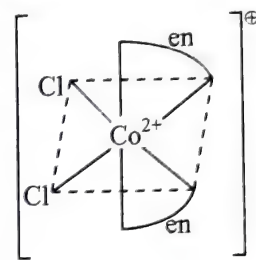


trans-isomer
(trans-meso form)

Mirror plane



cis-d-isomer



cis-l-isomer

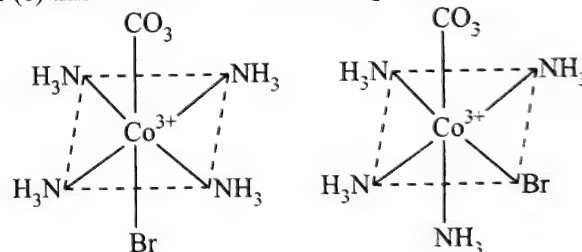
EXAMPLE 7.7

The formula $\text{Co}(\text{NH}_3)_4\text{CO}_3\text{Br}$ represents three isomers.

- Draw their structures
- How would you distinguish these isomers?

Sol.

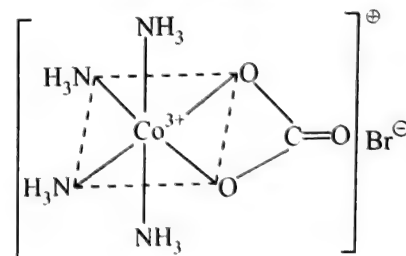
i. The structures of the three isomers represented by the given formula are given in the figure. In isomers (a) and (b), CO_3^{2-} ion acts as a monodentate ligand but in isomer (c) this ion acts as a bidentate ligand.



a. $(\text{CO}_3^{2-}-\text{Br}^\ominus)$ trans

b. $(\text{CO}_3^{2-}-\text{Br}^\ominus)$ cis

Non-ionic isomers



c. Ionic isomer

ii. These isomers can be distinguished by the following methods:

- Chemical method:** When isomer (c) is treated with AgNO_3 solution, yellow ppt. of AgBr is obtained.

- b. **Infra-red spectroscopic method:** The absorption spectra of isomers (a) and (b) are different from that of isomer (c), since in (a) and (b), CO_3^{2-} ion acts as a monodentate ligand but in (c) this ion acts as a bidentate ligands.

EXAMPLE 7.8

On the basis of VBT, answer the following questions for the 4-coordinated complex compounds

- a. $[\text{CoBr}_4]^{2-}$ b. $[\text{Zn}(\text{CN})_4]^{2-}$ c. $[\text{MnCl}_4]^{2-}$

- What is the oxidation state of the central metal atom/ion?
- What type of hybridisation is involved?
- What is the geometry and magnetic behaviour of the complex ion/compound?
- Calculate the value of μ_{spin} only.

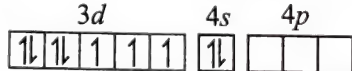
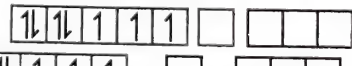
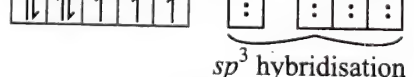
Sol.

- a. $[\text{CoBr}_4]^{2-}$:

- i. Let the oxidation state of Co in $[\text{CoBr}_4]^{2-}$ be x .

$$\begin{aligned} \text{Then, } x + (-1) \times 4 &= -2 \\ x &= -2 + 4 = +2 \end{aligned}$$

Therefore, oxidation state of Co in $[\text{CoBr}_4]^{2-}$ is +2.

- ii. Co atom ($3d^7 4s^2$) 
 Co²⁺ ion ($3d^7 4s^0$) 
 Co²⁺ ion in $[\text{CoBr}_4]^{2-}$ 

Br^- is a weak ligand, so no pairing of 3d electrons occurs.

- iii. Since Co^{2+} ion in $[\text{CoBr}_4]^{2-}$ shows sp^3 hybridisation, geometry of complex ion is tetrahedral, further as evident three unpaired electrons are present, so the complex ion is paramagnetic.

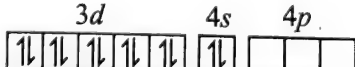
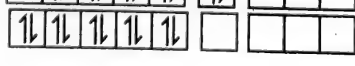
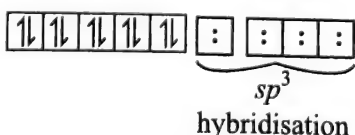
- iv. $\mu_{\text{spin}} = \sqrt{n(n+2)} \text{ BM}$

$$\begin{aligned} \mu_{\text{spin}} \text{ only} &= \sqrt{3(3+2)} = \sqrt{15} \quad (\because n=3) \\ &= 3.87 \text{ BM} \end{aligned}$$

- b. $[\text{Zn}(\text{CN})_4]^{2-}$ ion:

- i. Let oxidation state of Zn in $[\text{Zn}(\text{CN})_4]^{2-}$ be x

$$\begin{aligned} x + (-1) \times 4 &= -2 \\ x &= +2 \end{aligned}$$

- ii. Zn atom ($3d^{10} 4s^2$) 
 Zn²⁺ ion ($3d^{10} 4s^0$) 
 Zn²⁺ ion ($3d^{10} 4s^0$) in $[\text{Zn}(\text{CN})_4]^{2-}$ 

- iii. As evident, Zn^{2+} ion in $[\text{Zn}(\text{CN})_4]^{2-}$ is sp^3 hybridised, with no unpaired electrons, therefore geometry of $[\text{Zn}(\text{CN})_4]^{2-}$ is tetrahedral and it is diamagnetic.

$$\begin{aligned} \text{iv. } \mu_{\text{spin}} \text{ only} &= \sqrt{n(n+2)} \text{ BM} \\ n &= 0, \mu_{\text{spin}} \text{ only} = 0 \end{aligned}$$

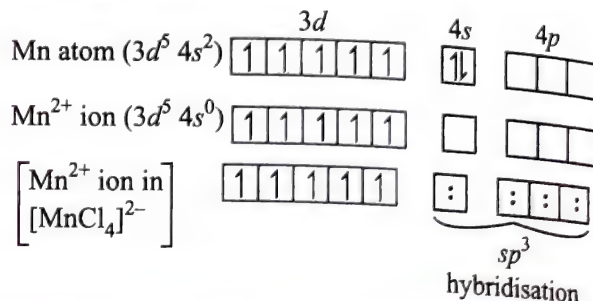
- c. $[\text{MnCl}_4]^{2-}$:

- i. Let, oxidation state of Mn in $[\text{MnCl}_4]^{2-}$ be x

$$\begin{aligned} x + (-1) \times 4 &= -2 \\ x &= +2 \end{aligned}$$

Therefore, oxidation state of Mn in $[\text{MnCl}_4]^{2-}$ is +2.

- ii. Electronic configuration of



Cl^- is a weak ligand, so no pairing of 3d electrons occurs.

- iii. Since Mn^{2+} ion is sp^3 hybridised in $[\text{MnCl}_4]^{2-}$, geometry of $[\text{MnCl}_4]^{2-}$ is tetrahedral. Magnetic behaviour of $[\text{MnCl}_4]^{2-}$ is paramagnetic ($n=5$).

$$\text{iv. } \mu_{\text{spin}} \text{ only} = \sqrt{5(5+2)} \text{ BM} = \sqrt{35} \text{ BM} = 5.91 \text{ BM}$$

EXAMPLE 7.9

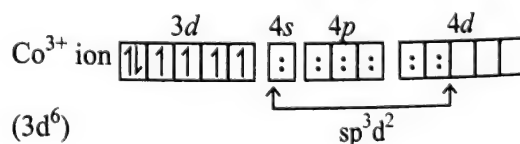
- Explain why a knowledge of magnetic susceptibility of a complex is often necessary for a correct assignment of the electronic configuration according to valence bond theory.
- Draw valence bond representations of the electronic structures of (i) $[\text{CoF}_6]^{3-}$ (paramagnetic) and (ii) $[\text{Co}(\text{CN})_6]^{3-}$ (diamagnetic)

Sol.

- a. Inner orbital complexes in which inner orbitals are involved i.e., d^2sp^3 or dsp^2 or dsp^3 , electron pairing is necessary in some cases. The change in magnetic susceptibility moment is an indication of what orbitals are being used.

- b. i. Valence bond representation of $[\text{CoF}_6]^{3-}$ (paramagnetic) Co is Co^{3+} ion in $[\text{CoF}_6]^{3-}$,

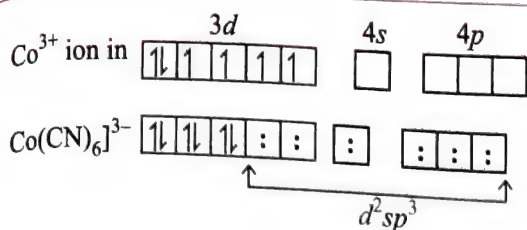
$$[\text{Co} (Z=27) \Rightarrow 3d^7 4s^2; \text{Co}^{3+} \Rightarrow 3d^6]$$



Since $[\text{CoF}_6]^{3-}$ is paramagnetic, electron pairing will not take place and Co^{3+} ion will be sp^3d^2 hybridised forming outer orbital complex.

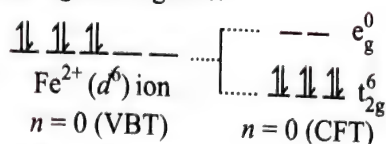
- ii. Valence bond representation of $[\text{Co}(\text{CN})_6]^{3-}$ (diamagnetic).

In $[\text{Co}(\text{CN})_6]^{3-}$, Co is present as Co^{3+}



Since the complex ion is diamagnetic pairing of electrons takes place, resulting in Co³⁺ ion in [Co(CN)₆]³⁻ complex ion to be d^2sp^3 hybridised and hence forms inner orbital complex.

In strong field ligands:



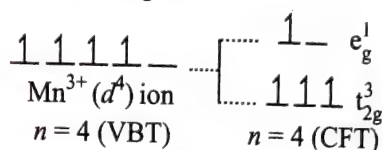
- ii. b. $\mu = 4.9$ BM corresponds to $n = 4$ and for $\mu = 2.80$ BM corresponds to $n = 2$.

For d^4 configuration, in a weak field ligands it will have 4 unpaired electrons. In strong field ligand, d^4 configuration will have one paired electrons and two unpaired electrons.

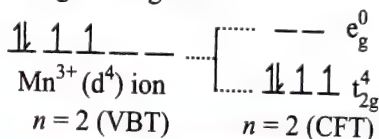
Note: d^1 to d^3 configuration, no pairing will occur whether the ligand field is weak or strong. But for d^4 configuration only one pairing will occur in strong field ligands

Therefore, Mn³⁺ have $3d^4$ configuration.

In weak field ligands:



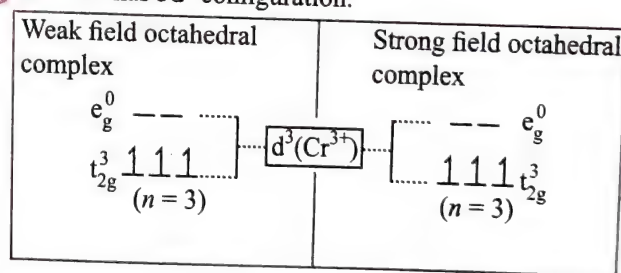
In strong field ligands:



EXAMPLE 7.12

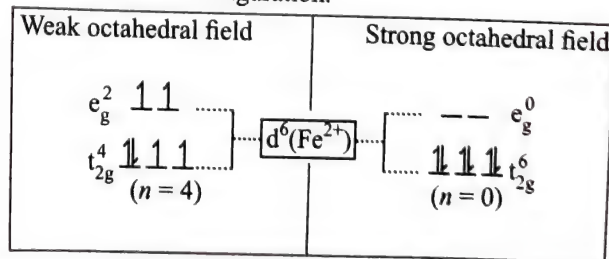
Find out the number of unpaired electrons in strong and weak octahedral field for Cr³⁺ and Fe²⁺ ions.

Sol. Cr³⁺ ion has $3d^3$ configuration.



Number of unpaired electrons, $n = 3$ (in both cases)

Fe²⁺ ion has $3d^6$ configuration.



Number of unpaired electrons; $n = 4$, in weak octahedral field, $n = 0$, in strong octahedral field.

EXAMPLE 7.13

Distinguish between the possibilities in complex ions of $\Delta = 0$ and CFSE = 0. Give an example of each.

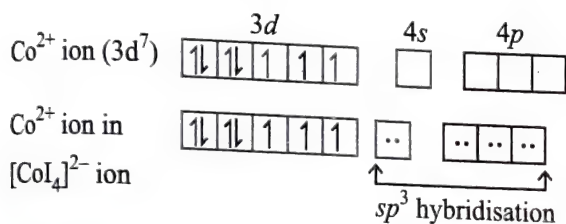
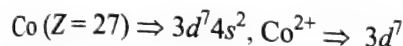
EXAMPLE 7.10

Magnetic moment of [CoI₄]²⁻ is 3.8 BM. Using valence bond approach, predict the structure of [CoI₄]²⁻.

Sol. $\mu_s = 3.80$ BM corresponds to $n = 3$.

∴ Number of unpaired electrons = 3

Coordination number (CN) and oxidation state (OS) of Co in the complex are 4 and +2 respectively.



Since the complex is paramagnetic with $n = 3$, electron pairing will not take place and Co²⁺ ion in the complex is tetrahedral.

EXAMPLE 7.11

i. A complex of a certain metal ion has a magnetic moment of 4.90 BM. Another complex of the same metal ion in the same oxidation state has a zero magnetic moment. The central metal ion could be which of the following?

- a. Cr³⁺ b. Mn³⁺ c. Fe²⁺ d. Co²⁺

ii. Refer to the question above, if a metal ion has complex ion and with magnetic moments 4.90 and 2.8 BM which one of these is the central metal ion.

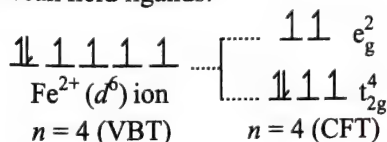
- a. Cr³⁺ b. Mn³⁺ c. Fe²⁺ d. Co²⁺

Sol.

i. c. $\mu = 4.90$ B.M. corresponds to $n = 4$ which corresponds d^6 configuration. In a weak field ligands, d^6 configuration will have 4 unpaired electrons. In strong field ligands, d^6 configuration will have no unpaired electrons with zero magnetic moment value.

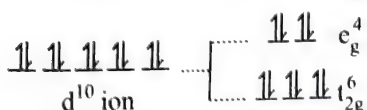
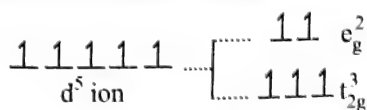
Fe²⁺ have $3d^6$ configuration.

In weak field ligands:



Sol. $\Delta = 0$ means no crystal field splitting i.e. case of free gaseous ion.

CFSE = 0 means equal occupancy of all the d -orbitals, i.e. d^5 weak field ion, and d^{10} both weak and strong field ion.



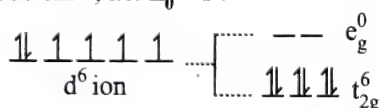
Example of case when $\Delta_0 = 0$, Zn^{2+} gaseous ion.

CFSE = 0 in $[Mn(H_2O)_6]^{2+}$ and $[Zn(H_2O)_6]^{2+}$

EXAMPLE 7.14

Determine the crystal field stabilisation energy of a d^6 complex having $\Delta_0 = 25000 \text{ cm}^{-1}$ and $P = 15000 \text{ cm}^{-1}$.

Sol. For d^6 complex, when $\Delta_0 = 25000 \text{ cm}^{-1}$ and $P = 15000 \text{ cm}^{-1}$, i.e. $\Delta_0 > P$.



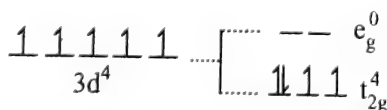
$$\begin{aligned} \text{CFSE} &= -(0.4 \times 6) \Delta_0 + 3P \\ &= -(0.4 \times 6) \times 25000 \text{ cm}^{-1} + 3 \times 15000 \text{ cm}^{-1} \\ &= -15000 \text{ cm}^{-1} \end{aligned}$$

EXAMPLE 7.15

On the basis of CFT, predict the geometry of the compound, $K_3[Mn(CN)_6]$. Also calculate the value of μ_{spin} only of the compound.

Sol. In $K_3[Mn(CN)_6]$, $[Mn(CN)_6]^{3-}$ is the complex ion. In $[Mn(CN)_6]^{3-}$ the oxidation state of central metal ion, i.e. Mn is +3. ($Mn = 3d^5 4s^2$, $Mn^{3+} = 3d^4$).

CN of Mn in $[Mn(CN)_6]^{3-}$ is 6, hence it is an octahedral complex. CN^- ion is a strong field ligands, therefore $[Mn(CN)_6]^{3-}$ is low spin octahedral complex and hence Mn^{3+} ion (in $[Mn(CN)_6]^{3-}$) is $t_{2g}^4 e_g^0$.



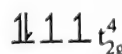
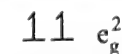
Splitting of d -orbitals in octahedral geometry with $n = 2$

$$\mu_{\text{spin}} = \sqrt{2(2+2)} = 2.83 \text{ BM}$$

EXAMPLE 7.16

The enthalpy of hydration of the Fe^{2+} ion is 11.4 kcal/mol higher than would be expected if there were no crystal field stabilisation energy. Assuming the aquo complex to be high spin, estimate the magnitude of Δ_0 for $[Fe(H_2O)_6]^{2+}$ ion.

Sol. Fe^{2+} is $t_{2g}^4 e_g^2$ in weak field environment



$$\begin{aligned} \text{CFSE} &= -(0.4 \times 4) \Delta_0 + (0.6 \times 2) \Delta_0 \\ &= -1.6 \Delta_0 + 1.2 \Delta_0 \\ &= -0.4 \Delta_0 \end{aligned}$$

ΔH_{hyd} is higher because the energy of the complex is lowered by -11.4 kcal/mol.

$$\text{CFSE} = -11.4 \text{ kcal/mol} = -0.4 \Delta_0$$

$$\Delta_0 = \frac{-11.4}{-0.4} = -28.5 \text{ kcal/mol}$$

EXAMPLE 7.17

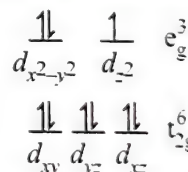
If a complexing metal of the first transition series has a d^i configuration for what values of 'i' could magnetic properties alone distinguish between strong field and weak field ligands in octahedral coordination?

Sol. When $i = 4, 5, 6$ and 7 , i.e. d^4, d^5, d^6 and d^7 configuration, magnetic values alone can distinguish between strong field and weak field ligands in octahedral coordination.

EXAMPLE 7.18

In terms of CFT, explain why a d^9 octahedral complex with six identical ligands is not expected to have all size M-L distances identical.

Sol. For d^9 octahedral complex, the configuration will be $t_{2g}^6 e_g^3$



One of the e_g orbitals is completely filled and other is half filled and hence interaction with the ligands is expected to be different.

EXAMPLE 7.19

Derive the geometry of the complex compound corresponding to the brown ring in nitrate test. Predict the magnetic moment of the complex.

Sol. Brown ring formed in the nitrate test is due to the formation of the complex ion $[Fe(H_2O)_5(NO)]^{2+}$ in which Fe and NO both are present as Fe^{\oplus} and NO^{\oplus} (nitrosonium) ions respectively. Fe^{\oplus} ion acts as the central metal ion and NO^{\oplus} ion acts as a ligand. Five H_2O molecules also act as ligands.

Since CN of Fe^{\oplus} ion is $5 + 1 = 6$, $[Fe(H_2O)_5(NO)]^{2+}$ is an octahedral complex ion which is formed by sp^3d^2 hybridisation and has 3 unpaired electrons (i.e. $n = 3$).

Thus $[Fe(H_2O)_5(NO)]^{2+}$ ion is paramagnetic and its

$$\mu = \sqrt{3 \times (3+2)} \text{ BM} = \sqrt{15} = 3.89 \text{ BM}$$

a.	Fe ($Z = 26$)	$3d^6 4s^2$			
b.	Fe ³⁺ ion is the complex ($3d^6 4s^1$)	$3d^6$ $\uparrow \uparrow \uparrow \uparrow \uparrow$	$4s^1$ \uparrow	$4p^0$ ---	$4d^0$ -----
c.	NO ⁺ is a strong field ligand so pairing of only 1 electron occurs. H ₂ O is a weak field ligand, so pairing does not occur with five H ₂ O ligands	$3d^7$ $\uparrow \uparrow \uparrow \uparrow \uparrow$	$4s^0$ —	$4p^0$ ---	$4d^0$ -----
d.	[Fe ³⁺ (H ₂ O) ₅ NO ⁺]	$3d^7$ $\uparrow \uparrow \uparrow \uparrow \uparrow$ ($n = 3$)	<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $4s$ <div style="border: 1px solid black; padding: 5px; display: inline-block;"> $\uparrow \downarrow$ NO⁺ </div> </div> <div style="text-align: center;"> $4p$ <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $\uparrow \downarrow$ O H₂ </div> <div style="text-align: center;"> $\uparrow \downarrow$ O H₂ </div> <div style="text-align: center;"> $\uparrow \downarrow$ O H₂ </div> </div> </div> <div style="text-align: center;"> $4d$ <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $\uparrow \downarrow$ O H₂ </div> <div style="text-align: center;"> $\uparrow \downarrow$ O H₂ </div> </div> </div> <div style="text-align: center;"> <div style="border: 1px solid black; padding: 5px; display: inline-block;"> --- </div> </div> </div> <div style="text-align: center; margin-top: 10px;"> $\swarrow \quad \searrow$ $sp^3 d^2$ hybridisation, outer orbital octahedral geometry </div>		

EXAMPLE 7.20

1. Which of the electronic configuration according to crystal field theory of the compound is correct [MnF₆]⁴⁻?

- a. $3(t_{2g}^5 e_g^0)$ b. $3(t_{2g}^3 e_g^2)$
c. $4(e_g^2 t_{2g}^3)$ d. $4(t_{2g}^3 e_g^2)$

Which of the electronic configuration according to crystal field theory of the compound Rh²⁺ with CN = 6 is correct when $\Delta > P$?

- a. $3(t_{2g}^6 e_g^1)$ b. $4(t_{2g}^6 e_g^1)$
c. $3(t_{2g}^5 e_g^1)$ d. $4(t_{2g}^5 e_g^2)$

According to crystal field theory, the electronic configuration of the [Cr(H₂O)₆]²⁺ ion, when ($\Delta < P$) (Δ = CFSE, P = Pairing energy).

- a. $3(t_{2g}^3 e_g^1)$ b. $4(t_{2g}^3 e_g^1)$
c. $3(e_g^1 t_{2g}^1)$ d. $3(e_g^3 t_{2g}^1)$

According to crystal field theory, the electronic configuration of the [FeCl₄]⁻ ion is

- a. $3(t_{2g}^3 e_g^2)$ b. $3(e^2 t_2^3)$
c. $4(t_2^3 e^2)$ d. $4(e^2 t_2^3)$

According to crystal field theory, the electronic configuration of the compound [Mn(CN)₄]²⁻ is ($\Delta > P$):

- a. $4(e^4 t_2^1)$ b. $3(e^2 t_2^3)$
c. $4(e^2 t_2^3)$ d. $3(e^4 t_2^1)$

Crystal field splitting energy (CFSE) for the complex [Cr(H₂O)₆]²⁺ is when ($\Delta < P$)

- a. $-1.2 \Delta_0$ b. $-0.6 \Delta_0$
c. $0.6 \Delta_0$ d. $1.2 \Delta_0$

Crystal field splitting energy (CFSE) for the complex [Cr(NH₃)₆]²⁺ is (when $\Delta > P$)

- a. $-1.6 \Delta_0 + P$ b. $1.6 \Delta_0 + P$
c. $-2.4 \Delta_0 + P$ d. $2.4 \Delta_0 + P$

8. Crystal field splitting energy (CFSE) for the complex [Cr(H₂O)₆]²⁺ is when $P = 20925 \text{ cm}^{-1}$ and $\Delta_0 = 10462.5 \text{ cm}^{-1}$ ($1 \text{ kJ mol}^{-1} = 83.7 \text{ cm}^{-1}$)

- a. -75 kJ mol^{-1} b. 75 kJ mol^{-1}
c. 750 kJ mol^{-1} d. -750 kJ mol^{-1}

9. Crystal field splitting energy (CFSE) for the complex [Cr(NH₃)₆]²⁺ is when $P = 125$ and $\Delta_0 = 250 \text{ kJ mol}^{-1}$

- a. 525 kJ mol^{-1} b. 275 kJ mol^{-1}
c. -275 kJ mol^{-1} d. -525 kJ mol^{-1}

10. In which structure crystal field splitting energy (CFSE) for octahedral complex will be zero when $\Delta < P$.

- a. d^5 b. d^6
c. d^8 d. d^9

11. In which structure crystal field splitting energy (CFSE) for octahedral complex will be minimum or zero when $\Delta > P$.

- a. d^5 b. d^6
c. d^8 d. d^{10}

12. Crystal field splitting energy (CFSE) for the complex [FeCl₄]⁻ is when $\Delta < P$.

- a. $-1.0 \Delta_t$ b. $1.0 \Delta_t$
c. 0 d. $-1.8 \Delta_t$

13. Crystal field splitting energy (CFSE) for the complex [Fe(CN)₄]⁻ is when $\Delta > P$.

- a. -2.0 b. $\Delta + P$
c. $2 + P$ d. 0

14. Crystal field splitting energy (CFSE) for the complex [FeO₄]²⁻ is when $\Delta = 125$ and $P = 250 \text{ kJ mol}^{-1}$.

- a. $-1.2 \Delta_t$ b. $1.2 \Delta_t$
c. -8 d. 8

15. CFSE for d^6 octahedral complex having $\Delta = 250$ and $P = 125 \text{ kJ mol}^{-1}$ is

- a. 350 kJ mol^{-1} b. -350 kJ mol^{-1}
c. 475 kJ mol^{-1} d. -475 kJ mol^{-1}

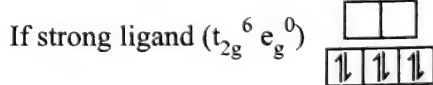
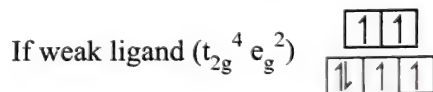
16. The enthalpy of hydration of Cr^{+2} is $-460 \text{ kcal mol}^{-1}$. In the absence of CFSE, the value for ΔH is $-424 \text{ kcal mol}^{-1}$. What is the value of Δ_0 for $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
- $60 \text{ kcal mole}^{-1}$
 - $-60 \text{ kcal mole}^{-1}$
 - $25.7 \text{ kcal mole}^{-1}$
 - $-25.7 \text{ kcal mole}^{-1}$

Sol.

Note: Pairing energy should be considered only for low spin complexes (strong ligand) because electron foresfully paired so pairing energy is required. But for high spin complexes (weak ligand), pairing energy is not considered because e^- 's pairs in natural way as like free metal ion.

- b.** Octahedral complex, CN = 6
Weak ligand (F^\ominus)
 $\text{Mn} = 3d^5 4s^2$, $\text{Mn}^{2+} = 3d^5$
 $\therefore 3(t_{2g}^3 e_g^2)$
- b.** $\text{Rh} = 4d^7 5s^2$ $\text{Rh}^{+2} = 4d^7$
When $\Delta > P$ (Strong field and pairing occurs)
Structure = $4(t_{2g}^6 e_g^1)$
- a.** Octahedral complex, when ($\Delta < P$) (weak field)
(high spin state) (No pairing)
 $\text{Cr} = 3d^5 4s^1$, $\text{Cr}^{+2} = 3d^4$ \therefore Structure = $3(t_{2g}^3 e_g^1)$
- b.** Tetrahedral complex, CN = 4.
Weak ligand (Cl^\ominus) (No pairing; High spin complex)
 $\text{Fe} = 3d^6 4s^2$, $\text{Fe}^{+3} = 3d^5$ \therefore Structure = $3(e^2 t_2^3)$
- b.** Tetrahedral complex, CN = 4
 $\text{Mn} = 3d^5 4s^2$, $\text{Mn}^{+2} = 3d^5$, $\Delta > P$
(Strong field but pairing does not take place, in tetrahedral complexes)
 \therefore Structure = $3(e^2 t_2^3)$
- b.** Octahedral complex, CN = 6, $\Delta < P$
(Weak ligand, no pairing, high spin state)
 $\text{Cr} = 3d^5 4s^1$, $\text{Cr}^{+2} = 3d^4$ Structure = $(t_{2g}^3 e_g^1)$
 $\text{CFSE} = (-0.4 \times 3 + 0.6) \Delta_0 = -0.6 \Delta_0$
- a.** Octahedral complex, CN = 6, $\Delta > P$
(Strong ligand, one pairing, low spin state)
 $\text{Cr} = 3d^5 4s^1$, $\text{Cr}^{+2} = 3d^4$ Structure is $3(t_{2g}^4 e_g^0)$
 $\text{CFSE} = (-0.4 \times 4) \Delta_0 + P = -1.6 \Delta_0 + P$
- a.** $\Delta < P$ (weak field, no pairing, high spin state)
Octahedral complex, CN = 6
 $\text{Cr} = 3d^5 4s^1$, $\text{Cr}^{+2} = 3d^4$ Structure is: $3(t_{2g}^3 e_g^1)$
 $P = \frac{20925 \text{ cm}^{-1}}{83.7} = 250 \text{ kJ mol}^{-1}$
 $\Delta_0 = \frac{10462.5 \text{ cm}^{-1}}{83.7} = 125 \text{ kJ mole}^{-1}$
 $\text{CFSE} = (-0.4 \times 3 + 0.6) \Delta_0 = -0.6 \Delta_0 = -0.6 \times 125$
 $= -75 \text{ kJ mol}^{-1}$

- c.** $\Delta > P$, strong field, pairing, low spin
Octahedral complex, CN = 6
 $\text{Cr} = 3d^5 4s^1$, $\text{Cr}^{+2} = 3d^4$ Structure is $3(t_{2g}^4 e_g^0)$
 $\text{CFSE} = (-0.4 \times 4) \Delta_0 + P = -1.6 \times 250 + 125$
 $= -275 \text{ kJ mol}^{-1}$
- a.** $\Delta < P$, weak field, no pairing, octahedral.
Structure of $d^5 = (t_{2g}^3 e_g^2) = -0.4 \times 3 + 2 \times 0.6 = 0$
- d.** If $\Delta < P$, weak field, no pairing $d^5 = t_{2g}^3 e_g^2$
 $\text{CFSE} = -0.4 \times 3 + 2 \times 1.6 = 0$
If $\Delta > P$, strong field, pairing $d^5 = t_{2g}^5 e_g^0$
 $\text{CFSE} = -0.4 \times 5 = -2 \Delta$
For d^{10} , $\Rightarrow t_{2g}^6 e_g^4 = -0.4 \times 6 + 0.6 \times 4 = 0$
- c.** Tetrahedral complex, CN = 4
($\Delta < P$ weak ligand, no pairing, high spin).
 $\text{Fe} = 3d^6 4s^2$, $\text{Fe}^{+3} = 3d^5$ Structure is $(e^2 t_2^3)$
 $\text{CFSE} = -0.6 \times 2 + 0.4 \times 3 = 0$
- d.** Tetrahedral complex, CN = 4, $\Delta > P$
Strong ligand, but pairing does not take place in tetrahedral complexes.
 $\text{Fe} = 3d^6 4s^2$ $\text{Fe}^{+3} = 3d^5 \Rightarrow (e^2 t_2^3)$
 $\text{CFSE} = (-0.6 \times 2 + 0.4 \times 3) \Delta_t = 0.0$
- a.** Tetrahedral complex, CN = 4, $\Delta < P$
Weak ligand, no pairing, high spin
 $\text{Fe} = 3d^6 4s^2$, $\text{Fe}^{+6} = 3d^2 \Rightarrow (e^2 t_2^0)$
 $\text{CFSE} = (-0.6 \times 2) \Delta_t = -1.2 \Delta_t$
- b.** Octahedral complex, $\Delta > P$ strong field, pairing, low spin. Structure is $(t_{2g}^6 e_g^0)$

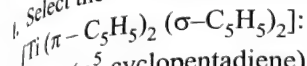


It means pairing energy is required for 2 electrons, since one pairing is already done in weak ligand
 $\text{CFSE} = (-0.4 \times 6) \Delta_0 + 2P = -2.4 \times 250 + 2 \times 125$
 $= -600 + 250 = -350 \text{ kJ mole}^{-1}$

- a.** $\text{Cr} = 3d^5 4s^1$, $\text{Cr}^{+2} = 3d^4$. Structure is $(t_{2g}^3 e_g^1)$
 $\text{CFSE} = (-0.4 \times 3 + 0.6) \Delta_0 = -0.6 \Delta_0$
 $-0.6 \Delta_0 = (-460) - (-424) = -36 \text{ kcal mol}^{-1}$
 $\Delta_0 = \frac{-36}{-0.6} = 60 \text{ kcal mol}^{-1}$
 $= 60 \times 350 \text{ cm}^{-1} = 21000 \text{ cm}^{-1}$
($1 \text{ kcal mol}^{-1} = 350 \text{ cm}^{-1}$)

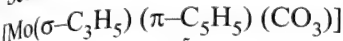
Terminology and Ligands

1. Select the correct IUPAC name for



- (1) bis (η^5 -cyclopentadiene) bis (cyclopentadiene) titanate(IV)
- (2) bis (η^5 -cyclopentadienyl) bis (cyclopentadienyl) titanium(IV)
- (3) bis (cyclopentadienyl) bis (η^5 -cyclopentadienyl) titanate(IV)
- (4) bis (η^5 -cyclopentadiene) bis (cyclopentadiene) titanium(IV)

2. Select the correct IUPAC name for



- (1) Tricarbonyl (η^5 -cyclopentadienyl) allyl molybdate(II)
- (2) Allyltricarbonyl (η^5 -cyclopentadiene) molybdate(II)
- (3) Allyltricarbonyl (η^5 -cyclopentadienyl) molybdenum(II)
- (4) Allyl tricarbonyl (η^5 -cyclopentadienyl) molybdenum(II)

3. IUPAC name for $[Fe(CO)_2(\sigma-C_5H_5)(\pi-C_5H_5)]$ complex:

- (1) Dicarbonyl (η^5 -cyclopentadienyl) (cyclopentadienyl) ferrate(II)
- (2) Dicarbonyl (η^5 -cyclopentadiene) (cyclopentadienyl) iron(II)
- (3) Dicarbonyl (η^5 -cyclopentadienyl) (cyclopentadienyl) iron(II)
- (4) Dicarbonyl (η^5 -cyclopentadienyl) (η^5 -cyclopentadienyl) iron(II)

4. Select the correct IUPAC name for $[Cr(C_6H_6)(CO)_3]$:

- (1) (η^6 -benzene) tricarbonylchromate(0)
- (2) Tricarbonyl (η^6 -benzene)chromate(0)
- (3) Tricarbonyl (η^6 -benzene)chromium(0)
- (4) (η^6 -benzene) tricarbonylchromium(0)

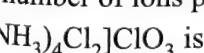
IUPAC name for complex $[Mn(\pi-C_6H_5)(CO)_3]$:

- (1) Tricarbonyl (η^5 -cyclopentadiene)manganese(I)
- (2) Tricarbonyl (η^5 -cyclopentadiene)manganate(I)
- (3) Tricarbonyl (η^5 -cyclopentadienyl)manganese(I)
- (4) (η^5 -cyclopentadienyl) tricarbonyl manganese(I)

Ligand with two or more points of attachment to single metal atoms are called:

- (1) Monodentate ligand
- (2) Chelating ligand
- (3) Ambidentate ligand
- (4) None of these

The number of ions produced by the complex



- (1) 2
- (2) 3
- (3) 4
- (4) 6

Which of the following is a tridentate ligand?

- (1) NO_2^\ominus
- (2) Oxalate ion
- (3) Glycinate ion
- (4) Dien

9. Coordination number of calcium is six in:

- (1) $[Mg(EDTA)]^{2-}$
- (2) MgC_2O_4
- (3) $[Mg(C_2O_4)_2]^{2-}$
- d. $MgSO_4 \cdot 4H_2O$

10. Coordination number of Cu^{2+} in $CuSO_4 \cdot 5H_2O$ is

- (1) 5
- (2) 4
- (3) 3
- (4) 2

11. The closed ring compounds formed by bidentate ligands, on binding to a metal or metal ions are called:

- (1) Monodentate
- (2) Chelates
- (3) Ambidentate
- (4) None of these

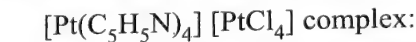
12. Which is the pair of ambidentate ligand?

- (1) CN^\ominus , NO_2^\ominus
- (2) NO_3^\ominus , SCN^\ominus
- (3) N_3^\ominus , NO_2^\ominus
- (4) NCS^\ominus , $C_2O_4^{2-}$

13. Number of water molecules acting as ligands in $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$ respectively are

- (1) 5, 5, 7
- (2) 4, 5, 4
- (3) 4, 4, 6
- (4) 4, 4, 7

14. Select the correct IUPAC name for



- (1) Tetrapyridineplatinate(II) tetrachloridoplatinate(II)
- (2) Tetrapyridineplatinate(II) tetrachloridoplatinum(II)
- (3) Tetrapyridineplatinate(II) tetrachloridoplatinum(II)
- (4) Tetrapyridineplatinum(II) tetrachloridoplatinate(II)

15. Select the correct IUPAC name for $[C_4H_4Fe(CO)_3]$ complex:

- (1) η^4 -cyclobutadiene tricarbonyliron(0)
- (2) Tricarbonyl (η^4 -cyclobutadienyl) iron(0)
- (3) Tricarbonyl (η^4 -cyclobutadiene) iron(1)
- (4) Tricarbonyl (η^4 -cyclobutadiene) iron(0)

16. Oxidation state of "V" in $Rb_4K[HV_{10}O_{28}]$ is

- (1) +5
- (2) +6
- (3) $+\frac{7}{5}$
- (4) +4

17. Coordination number of Cr is six. A complex with $C_2O_4^{2-}$, en and superoxide O_2^\ominus will be in the ratio to make complex $[Cr(C_2O_4)_x(en)_y(O_2)_z]^\ominus$

	x	y	z
(1)	1	1	1
(2)	1	1	2
(3)	1	2	2
(4)	2	1	1

18. The compound $[CoCl_3I(C_5H_5N)_2]Br$ will show the chemical test for which of the following ions?

- (1) Br^\ominus
- (2) Cl^\ominus
- (3) I^\ominus
- (4) Br^\ominus as well as Cl^\ominus

19. The correct IUPAC name of $[Mn_3(CO)_{12}]$ is

- (1) Dodecacarbonylmanganate(0)
- (2) Dodecacarbonylmanganic(II)

- (3) Dodecacarbonyltrimanganese(0)
 (4) Manganiododecarbonyl(0)
20. The correct name of $(\text{CO})_3\text{Fe} \begin{array}{c} \diagup \text{CO} \diagdown \\ \text{CO} \\ \diagdown \text{CO} \diagup \end{array} \text{Fe}(\text{CO})_3$ is
 (1) Tri- μ -carbonylbis(tricarbonyl iron(0))
 (2) Hexacarbonyliron(III) μ -tricarbonylferrate(0)
 (3) Tricarbonyliron(0) μ -tricarbonyliron(0)
 (4) Nonacarbonyl iron
21. The correct IUPAC name of the complex:

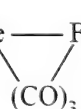
$$\begin{array}{c} \text{OH} \\ | \\ \text{H}_3\text{C}-\text{C}=\text{N} \nearrow \\ | \quad \quad \quad \searrow \\ \text{H}_3\text{C}-\text{C}=\text{N} \nearrow \text{CoCl}_2 \\ | \\ \text{OH} \end{array}$$

 (1) Dichloridodimethylglyoximatocobalt(II)
 (2) Bis(dimethylglyoxime) dichlorocobalt(II)
 (3) Dimethylglyoximecobalt(II) chloride
 (4) Dichloridodimethylglyoxime-N,N-cobalt(II)
22. The correct IUPAC name of $[\text{AlCl}_3] \cdot 4(\text{EtOH})$ is
 (1) Aluminium(II) chloride-4-ethanol
 (2) Trichloridoaluminium(III)-4-ethanol
 (3) Aluminium(III) chloride-4-hydroxyethane
 (4) Aluminium chloride-4-ethanol
23. In octaamine- μ -dihydroxodiiron(III) sulphate, the number of bridging ligands is
 (1) 2 (2) 1
 (3) 3 (4) None
24. The IUPAC name of the complex having formula $[(\text{CO})_3\text{Fe}(\text{CO})_3\text{Fe}(\text{CO})_3]$ is
 (1) Monocarbonylferrate(0)
 (2) Tricarbonyliron(0)- μ -tricarbonyliron(0)
 (3) Tri- μ -carbonylbis-{tricarbonyliron(0)}
 (4) Hexacarbonyl- μ -tricarbonyliron(III)
25. A group of atoms can function as a ligand only when
 (1) It is a small molecule
 (2) It is capable of acting as donor of electron pair
 (3) It is a negatively charged ion
 (4) It is a positively charged ion.
26. Which of the following is most likely structure of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ if 1/3 of total chlorine of the compound is precipitated by adding AgNO_3 to its aqueous solution?
 (1) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (2) $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] (\text{H}_2\text{O})_3$
 (3) $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ (4) $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$
27. The coordination number of the central ion may be obtained from
 (1) The number of ionic bonds formed with the surrounding ions
 (2) The number of coordinate bonds formed with the surrounding atoms
 (3) The number of ions of opposite charge immediately surrounding the specific ion
 (4) None of the above
28. Which of the following is nonionisable?
 (1) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (2) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
 (3) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (4) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
29. Which of the following pair contains complex salt and double salt respectively?
 (1) FeSO_4 , $\text{K}_4[\text{Fe}(\text{CN})_6]$
 (2) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
 (3) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, $\text{K}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
 (4) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
30. In which of the following compounds the metal is in the lowest oxidation state?
 (1) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ (2) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
 (3) $[\text{Mn}_2(\text{CO})_{10}]$ (4) $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$
31. Which of the following can be termed as mixed complex?
 (1) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (2) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
 (3) $[\text{Co}(\text{NH}_3)_4\text{NO}_2\text{Cl}]\text{Cl}$ (4) K_2FeSO_4
32. The oxidation number of Co in $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$ is
 (1) +2 (2) +1
 (3) +3 (4) +6
33. The IUPAC name for the coordination compound $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$ is
 (1) Sodium silverthiosulphate(I)
 (2) Sodium silverhyposulphate(I)
 (3) Sodium bis[argentothiosulphate(I)]
 (4) Sodium bis(thiosulphato)argentite
34. The IUPAC name for the coordination compound $[\text{CuCl}_2(\text{CH}_3\text{NH}_2)_2]$ is
 (1) Dimethylamine copper(II) chloride
 (2) Bis(dimethylamine copper(II) chloride
 (3) Dichloridobis(methylamine) copper(II)
 (4) Dichlorobis(dimethylamine) copper(II)
35. The IUPAC name for $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ is
 (1) Pentahydroaluminium hydroxide
 (2) Aquometaaluminate ion
 (3) Pentaquaaluminate(III) hydroxide
 (4) Pentaquaahydroxoaluminium(III)
36. The IUPAC name for $[\text{Pt}(\text{Br})(\text{Cl})(\text{NH}_3)_3(\text{NO}_2)]\text{Cl}$ is
 (1) Triamminechloridobromidonitroplatinum(IV) chloride
 (2) Triamminebromidochloridonitroplatinum(IV) chloride
 (3) Triamminnitrochlorobromoplatinum(IV) chloride
 (4) Triamminechloronitrobromoplatinum(IV) chloride
37. The oxidation number of Cr in $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ is
 (1) 0 (2) +2
 (3) +3 (4) +6
38. Which of the following has five donor (coordinating) sites?
 (1) Ethylenediaminetriacetate ion
 (2) Diethylene triamine
 (3) Ethylenediaminetetracetate ion
 (4) Triethylene tetramine.

39. Which of the following is not chelating agent?
 (1) Thiosulphate (2) Oxalato
 (3) Glycinato (4) Ethylene diamine
40. The solution of AgBr in presence of large excess of NH_3 contains mainly the cation.
 (1) NH_4^+ (2) Ag^+
 (3) $[\text{Ag}(\text{NH}_3)]^+$ (4) $[\text{Ag}(\text{NH}_3)_2]^+$
41. Which of the following species is not expected to be a ligand?
 (1) NO^+ (2) NH_4^+
 (3) $\text{NH}_2 - \text{NH}_3^+$ (4) CO
42. The number of donor sites in dimethyl glyoxime, glycinato, diethylene triamine and EDTA are respectively:
 (1) 2, 2, 3 and 4 (2) 2, 2, 3 and 6
 (3) 2, 2, 2 and 6 (4) 2, 3, 3 and 6
43. Which of the following is a double salt?
 (1) Alum (2) Chrome alum
 (3) Microcosmic salt (4) All of these
44. When potash alum is dissolved in water the total number of ions produced is
 (1) Four (2) Eight
 (3) Ten (4) Thirty-two
45. Which of the following statements is correct with regard to a complex ion?
 (1) A complex ion consists of a central ion bonded to two or more donor ions or molecules, usually does not dissociate into simple ions or molecules even in a solution, and exhibits properties different from its constituent ions or molecules.
 (2) The donor ions and molecules which coordinate with the central atom or ion in a complex are called ligands.
 (3) The sum of the number of electrons present in the central metal ion or atom and those donated by the ligands is called the effective atomic number of the central metal atom and this number is usually the same as the atomic number of the next higher noble gas.
 (4) All of these
46. How many moles of AgCl would be obtained, when 100 mL of 0.1 M $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ is treated with excess of AgNO_3 ?
 (1) 0.01 (2) 0.02
 (3) 0.03 (4) None of these
47. 0.001 mol of $\text{Cr}(\text{NH}_3)_5(\text{NO}_3)(\text{SO}_4)$ was passed through a cation exchanger and the acid coming out of it required 20 mL of 0.1 M NaOH for neutralisation. Hence, the complex is
 (1) $[\text{Cr}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$ (2) $[\text{Cr}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$
 (3) $[\text{Cr}(\text{NH}_3)_5](\text{SO}_4)(\text{NO}_3)$ (4) None of these

Effective Atomic Number (EAN)

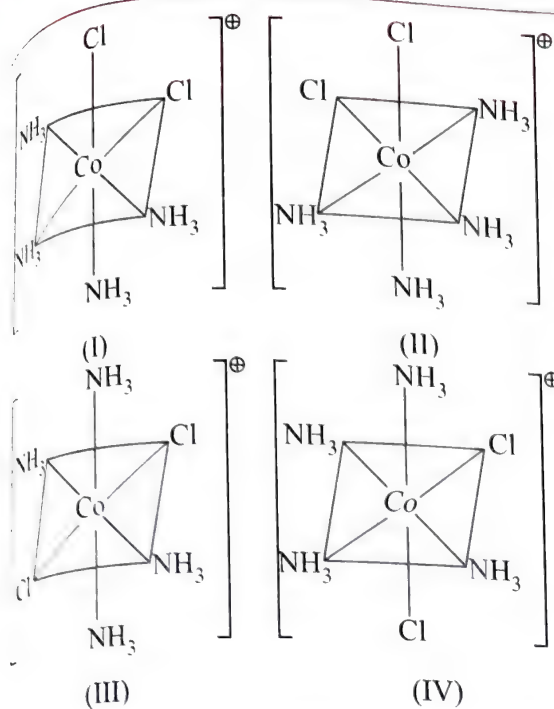
48. Among the following, select the order of decreasing EAN values
 I. $[\text{Cr}(\text{CO})_6]$
 II. $[\text{Cr}(\text{CO})_6]^\ominus$
 III. $[\text{Cr}(\text{CO})_6]^\oplus$

- (1) I > II > III (2) III > II > I
 (3) II > I > III (4) II = I > III
49. Increasing order EAN of the metals in
 I. $[\text{Ni}(\text{CN})_4]^{2-}$ II. $[\text{Fe}(\text{CN})_6]^{3-}$
 III. $[\text{Cu}(\text{CN})_4]^{3-}$ is
 (1) I < II < III (2) I < II = III
 (3) I < III < II (4) III < II < I
50. EAN of $\text{Na}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]$ is
 (1) 86 (2) 78
 (3) 84 (4) 34
51. EAN of $[\text{Fe}(\eta^2\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$:
 (1) 36 (2) 35
 (3) 37 (4) 34
52. Which has maximum EAN of the **underbold** atoms?
 (Cr = 24, Co = 27, Fe = 26, Ni = 28)
 (1) $[\text{Cr}(\text{EDTA})]^\ominus$ (2) $[\text{Co}(\text{en})_3]^{3+}$
 (3) $[\text{Ni}(\text{CN})_4]^{2-}$ (4) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
53. Give EAN value of Mg in $[\text{Mg}(\text{EDTA})]^{2-}$:
 (1) 16 (2) 20
 (3) 22 (4) 18
54. EAN of cobalt is 36 in $[\text{Co}(\text{NH}_3)_2\text{O}_2(\text{en})\text{Br}]$. Thus, O_2 is
 (1) dioxide (2) superoxide ion
 (3) peroxide ion (4) oxide
55. EAN of Fe in $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ is
 (1) 27 (2) 24
 (3) 35 (4) 29
56. The EAN of Fe atom in $(\text{CO})_3\text{Fe} - \text{Fe}(\text{CO})_3$ is

 (1) 34 (2) 35
 (3) 36 (4) 37

Isomerism

57. $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ are
 (1) Linkage isomers (2) Ionisation isomers
 (3) Coordination isomers (4) None of these
58. The type of isomerism present in pentaammine nitro chromium(III) perchlorate is
 (1) Optical (2) Linkage
 (3) Hydrate (4) Polymerisation
59. Which one of the following has the largest number of isomers?
 (1) $[\text{Cr}(\text{en})_2\text{Cl}_2]^\oplus$ (2) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$
 (3) $[\text{Ru}(\text{NH}_3)_4\text{Cl}_2]^\oplus$ (4) $[\text{Ir}(\text{PR}_3)_2\text{H}(\text{CO})]^{2+}$
60. $[\text{Cr}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$ and $[\text{Cr}(\text{NH}_3)_5\text{ONO}]\text{SO}_4$ are related to each other as:
 (1) Geometrical isomers (2) Linkage isomers
 (3) Coordination isomers (4) Ionisation isomers
61. Which one of the following will be able to show geometrical isomerism if complexes are square planar?
 (1) Ma_4 (2) Ma_3b
 (3) Mabcd (4) $[\text{M}(\text{AA})_2]$

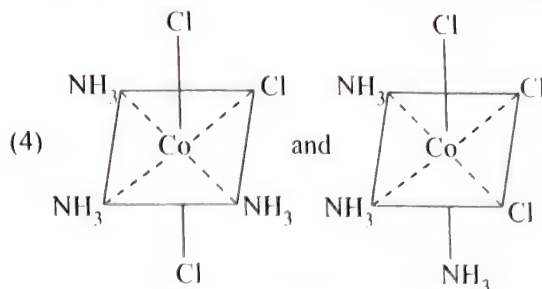
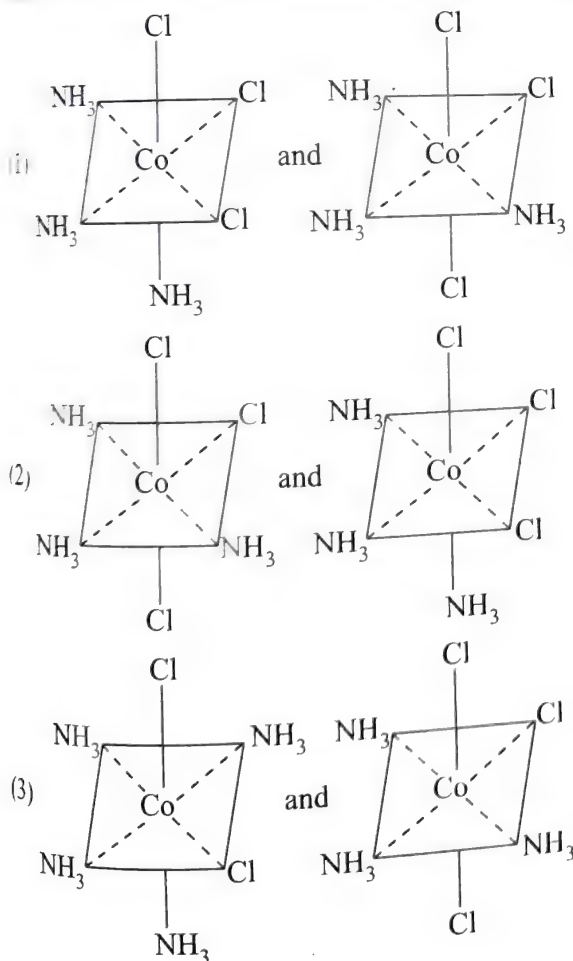
62. The number of geometrical and optical isomers of $[\text{Cr}(\text{NH}_3)_3(\text{NO}_3)_3]$ is
 (1) 3 (2) 2
 (3) 0 (4) 4
63. Both geometrical and optical isomerisms are shown by
 (1) $[\text{Co}(\text{en})_2\text{I}_2]^{\oplus}$ (2) $[\text{Co}(\text{NH}_3)_2\text{I}]^{2+}$
 (3) $[\text{Cr}(\text{OX})_3]^{3-}$ (4) $[\text{Co}(\text{NH}_3)_4\text{I}_2]^{\oplus}$
64. In $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$, the isomerism shown is
 (1) Ligand (2) Optical
 (3) Geometrical (4) Ionisation
65. Which of the following octahedral complex does not show geometrical isomerism (A and B are monodentate ligands)?
 (1) $[\text{MA}_3\text{B}_3]$ (2) $[\text{MA}_4\text{B}_2]$
 (3) $[\text{MA}_5\text{B}]$ (4) $[\text{MA}_2\text{B}_4]$
66. Facial-meridional isomerism is associated with which one of the following complex? (M = central metal)
 (1) $[\text{M}(\text{AA})_2]$ (2) $[\text{MA}_3\text{B}_3]$
 (3) $[\text{MABCD}]$ (4) $[\text{M}(\text{AA})_3]$
67. The total number of possible coordination isomer for the given compound $[\text{Pt}(\text{NH}_3)_4\text{Br}_2][\text{PtBr}_4]$ is
 (1) 2 (2) 4
 (3) 5 (4) 3
68. The following complexes are given
 1. $\text{trans}-[\text{Co}(\text{NH}_3)_4\text{I}_2]^{\oplus}$ 2. $\text{cis}-[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$
 3. $\text{trans}-[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$
 4. $[\text{NiI}_4]^{2-}$
 5. $[\text{TiF}_6]^{2-}$
 6. $[\text{CoF}_6]^{3-}$
 Choose the correct code.
 (1) 4, 5 are coloured; 6 is colourless
 (2) 2 is optically active; 1, 3 are optically inactive
 (3) 1, 2 are optically active; 3 optically inactive
 (4) 4 is coloured; 5, 6 are colourless
69. The following represents a pair of enantiomers:
 (1) $\text{trans}-[\text{CrI}_2\text{en}_2]^{\oplus}$ (2) $\text{cis}-[\text{CrI}_2\text{en}_2]^{\oplus}$
 (3) $\text{trans}-[\text{CrI}_2(\text{NH}_3)_4]^{\oplus}$ (4) $\text{cis}-[\text{CrI}_2(\text{NH}_3)_4]^{\oplus}$
70. The compound $[\text{PtBr}_2(\text{NH}_3)_2]$ can form
 (1) Geometrical isomers (2) Coordination isomers
 (3) Optical isomers (4) Linkage isomers
71. The compound $[\text{CrCl}_2(\text{NH}_3)_2(\text{en})]$ can form
 (1) Geometrical isomers (2) Coordination isomers
 (3) Optical isomers (4) Linkage isomers
72. One mole of complex compound $\text{Cr}(\text{NH}_3)_5\text{Cl}_3$ gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of AgNO_3 to yield two moles of $\text{AgCl}_{(s)}$. The complex is
 (1) $[\text{Cr}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2 \cdot \text{NH}_3$ (2) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$
 (3) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (4) $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3] \cdot 2\text{NH}_3$
73. Which of the following will show optical isomerism?
 (1) $[\text{ZnCl}_4]^{2-}$ (2) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (3) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ (4) $[\text{Co}(\text{CN})_6]^{3-}$
74. In which of the following pairs both the complexes show optical isomerism?
 (1) $\text{cis}-[\text{Cr}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{3-}$, $\text{cis}-[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$
 (2) $[\text{Co}(\text{en})_3]\text{Cl}_3$, $\text{cis}-[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$
 (3) $[\text{Co}(\text{NO}_3)_3(\text{NH}_3)_3]$, $\text{cis}-[\text{Pt}(\text{en})_2\text{Cl}_2]$
 (4) $[\text{PtCl}(\text{en})\text{Cl}]$, $[\text{NiCl}_2\text{Br}_2]^{2-}$
75. Which of the following gives the maximum number of isomers?
 (1) $[\text{Co}(\text{NH}_3)_4\text{I}_2]$ (2) $[\text{Ni}(\text{en})(\text{NH}_3)_4]^{2+}$
 (3) $[\text{Ni}(\text{C}_2\text{O}_4)(\text{en})_2]$ (4) $[\text{Cr}(\text{SCN})_2(\text{NH}_3)_4]^{\oplus}$
76. The possible number of optical isomers in $[\text{Cr}(\text{en})_2\text{Cl}_2]^{\oplus}$ is
 (1) 6 (2) 3
 (3) 4 (4) 2
77. Which of the following does not have optical isomers?
 (1) $[\text{Co}(\text{en})_3]\text{Br}_3$ (2) $[\text{Co}(\text{NH}_3)_3\text{Br}_3]$
 (3) $[\text{Co}(\text{en})_2\text{Br}_2]\text{Br}$ (4) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Br}_2]\text{Br}$
78. Which of the following will give a pair of enantiomorphs?
 (1) $[\text{Cr}(\text{NH}_3)_6]$ $[\text{Co}(\text{CN})_6]$ (2) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$
 (3) $[\text{Pt}(\text{NH}_3)_4]$ $[\text{PtCl}_6]$ (4) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$
79. Both Cr^{3+} and Pt^{4+} have a coordination number of 6. Which of the following pairs of complexes will show approximately the same electrical conductance for their 0.1 M aqueous solutions?
 (1) $\text{CrCl}_3 \cdot 4\text{NH}_3$ and $\text{PtCl}_4 \cdot 4\text{NH}_3$
 (2) $\text{CrCl}_3 \cdot 3\text{NH}_3$ and $\text{PtCl}_4 \cdot 5\text{NH}_3$
 (3) $\text{CrCl}_3 \cdot 6\text{NH}_3$ and $\text{PtCl}_4 \cdot 5\text{NH}_3$
 (4) $\text{CrCl}_3 \cdot 5\text{NH}_3$ and $\text{PtCl}_4 \cdot 6\text{NH}_3$
80. Select the correct statement for $[\text{M}(\text{AB})_2\text{b}_2\text{cd}]$:
 (1) All geometrical isomers are optically active.
 (2) It has four trans isomer with respect to b.
 (3) It has seven geometrical isomers.
 (4) It has three cis and two trans isomers with respect to b.
81. Which one of the following coordination compounds exhibits ionisation isomerism?
 (1) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (2) $[\text{Cr}(\text{en})_3]\text{Cl}_3$
 (3) $[\text{Cr}(\text{en})_3]\text{Cl}_3$ (4) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$
82. Which of the following complex compounds exhibits cis-trans isomerism?
 (1) $[\text{PtCl}_2(\text{NH}_3)_2]$ (2) $[\text{PdCl}_2\text{BrI}]$
 (3) $[\text{Pt}(\text{NH}_3)(\text{py})(\text{Cl})(\text{Br})]$ (4) All of these
83. How many geometrical isomers are possible for the square planar complex $[\text{Pt}(\text{NO}_2)(\text{py})(\text{NH}_3)(\text{NH}_2\text{OH})]\text{NO}_2^{\oplus}$?
 (1) Four (2) Five
 (3) Eight (4) Three
84. Consider the following spatial arrangements of the octahedral complex ion $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{\oplus}$.



Which of the following statements is **incorrect** regarding these structures?

- (1) I and II are enantiomers
- (2) II and III are *cis* and *trans* isomers respectively
- (3) III and IV are *trans* and *cis* isomers respectively
- (4) II and IV have identical structures.

Which of the following pairs of structures represent facial and meridional isomers (geometrical isomers) respectively?



86. Which would exhibit coordination isomerism?
 - (1) $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ (2) $[\text{Cr}(\text{en})_2\text{Cl}_2]^{\oplus}$
 - (3) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (4) $[\text{Cr}(\text{edta})]^{-1}$
87. Which would exhibit ionisation isomerism?
 - (1) $[\text{Co}(\text{NH}_3)_6][(\text{C}_2\text{O}_4)_3]$ (2) $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} \text{SO}_4^{2-}$
 - (3) $\text{K}_3[\text{Fe}(\text{CN})_6]$ (4) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
88. The water-soluble complex among the following is
 - (1) $[\text{Ni}(\text{HDMG})_2]$ (2) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
 - (3) $\text{Ni}(\text{CO})_4$ (4) $[\text{Ni}(\text{HDMG})_2]\text{Cl}_2$
89. Arrange the following optical activity possible in
 - (1) $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_3\text{Cl}]^{\oplus}$ (2) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]^{\oplus}$
 - (3) $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]^{\oplus}$ (4) $[\text{Co}(\text{CN})_5\text{NC}]^{\ominus}$
90. When an excess of ammonia solution is added to CuSO_4 which solution is formed?
 - (1) $[\text{Cu}(\text{NH}_3)_2]^{2+}$ (2) $[\text{Cu}(\text{NH}_3)_4]^{\oplus}$
 - (3) $[\text{Cu}(\text{NH}_3)_2]^{\oplus}$ (4) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
91. Copper sulphate solution reacts with KCN to give
 - (1) $\text{Cu}(\text{CN})_2$ (2) CuCN
 - (3) $\text{K}_2[\text{Cu}(\text{CN})_4]$ (4) $\text{K}_3[\text{Cu}(\text{CN})_4]$
92. The ionisation isomer of $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$ is
 - (1) $[\text{Co}(\text{H}_2\text{O})_4(\text{NO}_2)]\text{Cl}_2$ (2) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{NO}_2$
 - (3) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$ (4) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)] \cdot \text{H}_2\text{O}$
93. The 0.0001 molal solution of a complex AB_{10} has the freezing point of -0.0015°C in water. Assuming 100% dissociation of the complex, find the proper representation of the complex. $[\text{K}_f(\text{H}_2\text{O}) = 1.86 \text{ K m}^{-1}]$
 - (1) $[\text{AB}_8]$ (2) $[\text{AB}_3]\text{B}_7$
 - (3) $[\text{AB}_7]\text{B}_3$ (4) $[\text{AB}_5]\text{B}_5$
94. From the information given in the passage, what is the most likely configuration of the cobalt d-electrons for the species (A) CoCl_6^{3-} and (B) $\text{Co}(\text{NO}_2)_6^{3-}$?
 - (1) both (A) and (B) have low spin
 - (2) (A) has high spin; (B) has low spin
 - (3) (A) has low spin; (B) has high spin
 - (4) Both (A) and (B) have high spin
95. The hybridisation states of the central atom ion in the complex ions $[\text{FeF}_6]^{3-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$ are:
 - (1) sp^3d^2 , dsp^2 and d^4s^2 respectively
 - (2) all $3d^2 4s 4p^3$
 - (3) all $4s 4p^3 4d^2$
 - (4) sp^3d^2 , dsp^3 and p^4d^2 respectively

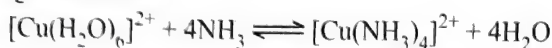
96. Among (A) TiF_6^{2-} , (B) CoF_6^{3-} , (C) Cu_2Cl_2 and (D) NiCl_4^{2-} (atomic number of Ti = 22, Co = 27, Cu = 29, Ni = 28), the colourless species are:

- (1) (B) and (D) (2) (A) and (B)
(3) (C) and (D) (4) (A) and (C)

97. The magnetic moment of a complex ion is 2.83 BM. The complex ion is:

- (1) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (2) $[\text{Cu}(\text{CN})_6]^{2-}$
(3) $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ (4) $[\text{MnCl}_4]^{2-}$

98. Which of the following statements is not true for the reaction given below?



- (1) It is a ligand-substitution reaction
(2) NH_3 is a relatively strong-field ligand while H_2O is a weak field ligand.
(3) During the reaction, there is a change in colour from light blue to dark blue.
(4) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ has a tetrahedral structure, and is paramagnetic.

Hybridisation, Magnetic and Optical Properties

99. The d -electron configurations of Mn^{2+} , Fe^{2+} , Co^{3+} and Ni^{2+} are $3d^5$, $3d^6$, $3d^6$, $3d^8$, respectively. Which of the following aqua complexes will exhibit the minimum paramagnetic behaviour?

- (1) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
(3) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (4) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

100. Which of the following is paramagnetic?

- (1) $[\text{Fe}(\text{CO})_5]$ (2) $[\text{Cr}(\text{CO})_6]$
(3) $[\text{Fe}(\text{CN})_6]^{4-}$ (4) $[\text{Cr}(\text{NH}_3)_6]^{3+}$

101. The pair in which both species have same magnetic moment (spin only value) is

- (1) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, $[\text{CoCl}_4]^{2-}$
(2) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
(3) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
(4) $[\text{CoCl}_4]^{2-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

102. Select the correct order of magnetic moment (in BM) from the following options:

- I. $[\text{MnCl}_4]^{2-}$ II. $[\text{CoCl}_4]^{2-}$ III. $[\text{Fe}(\text{CN})_6]^{4-}$
(1) I > II > III (2) III > II > I
(3) III > I > II (4) I > III > II

103. Which of the pair of complex compounds are tetrahedral as well as diamagnetic?

- (1) $[\text{CoCl}_4]^\ominus$ and $[\text{Co}(\text{CO})_4]^\ominus$
(2) $[\text{Ag}(\text{SCN})_4]^2$ and $[\text{NiCl}_4]^2$
(3) $[\text{Co}(\text{CO})_4]^\ominus$ and $[\text{Ni}(\text{CN})_4]^4$
(4) $[\text{PdCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^2$

104. Which of the following has a square planar geometry?

- (1) $[\text{PtCl}_4]^{2-}$ (2) $[\text{CoCl}_4]^{2-}$
(3) $[\text{FeCl}_4]^{2-}$ (4) $[\text{NiCl}_4]^{2-}$

105. Among $[\text{Ni}(\text{CO})_4]$, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiBr}_4]^{2-}$ species, the hybridisation state of Ni atoms are respectively:

- (1) sp^3 , ds^2p , dsp^2 (2) sp^3 , dsp^2 , sp^3
(3) dsp^2 , sp^3 , sp^3 (4) sp^3 , sp^3 , dsp^2

106. Arrange the following in order of decreasing number of unpaired electrons.

- I. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ II. $[\text{Fe}(\text{CN})_6]^{3-}$
III. $[\text{Fe}(\text{CN})_6]^{4-}$ II. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
(1) IV, I, II, III (2) I, II, III, IV
(3) III, II, I, IV (4) II, III, I, IV

107. A substance which is not paramagnetic is

- (1) $\text{Cr}(\text{ClO}_4)_3$ (2) KMnO_4
(3) TiCl_3 (4) VOBr_2

108. Which of the following statements is correct?

- (1) $[\text{NiCl}_4]^{2-}$ complex is more stable than $[\text{Ni}(\text{dmg})_2]$ due to higher CFSE value.
(2) With d^2sp^3 hybridisation $[\text{FeCl}(\text{CN})_4(\text{O}_2)]^{4-}$ complex is diamagnetic.
(3) $[\text{V}(\text{CO})_6]$ is not very stable and easily reduces to $[\text{V}(\text{CO})_6]^\ominus$.
(4) Ligands such as CO , CN^\ominus , NO^\oplus are π electron donor due to the presence of filled π -molecular orbital.

109. An aqueous solution of titanium bromide shows zero magnetic moment. Assuming the complex as octahedral in aqueous solution, the formula of the complex is

- (1) $[\text{TiBr}_6]^{3-}$ (2) $[\text{Ti}(\text{H}_2\text{O})_6]\text{Br}_4$
(3) $[\text{TiBr}_6]^{2-}$ (4) $[\text{Ti}(\text{H}_2\text{O})_4]\text{Br}_2$

110. Geometry, hybridisation and magnetic moment of the ions $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{MnBr}_4]^{2-}$, and $[\text{FeF}_6]^{3-}$, respectively are

- (1) Tetrahedral, square planar, octahedral:
 dsp^2 , sp^3 , sp^3d^2 : 0, 5.9, 4.9.
(2) Tetrahedral, square planar, octahedral:
 sp^3 , dsp^2 , sp^3d^2 : 5.9, 0, 4.9.
(3) Square planar, tetrahedral, octahedral:
 dsp^2 , sp^3 , d^2sp^3 : 5.9, 4.9, 0
(4) Square planar, tetrahedral, octahedral:
 dsp^2 , sp^3 , sp^3d^2 : 0, 5.9, 4.9

111. The correct order of magnetic moment (spin values in BM) is (Atomic number Mn = 25, Fe = 26, Co = 27)

- I. $[\text{MnBr}_4]^{2-}$ II. $[\text{Fe}(\text{CN})_6]^{4-}$ III. $[\text{CoBr}_4]^{2-}$
(1) II > III > I (2) I > II > III
(3) II > I > III (4) I > III > II

112. A square planar complex is formed by hybridisation of which atomic orbitals?

- (1) s , p_x , p_y , d_{z^2} (2) s , p_x , p_y , $d_{x^2-y^2}$
(3) s , p_y , p_z , d_{xy} (4) s , p_x , p_y , d_{z^2}

113. The colour of a complex compound is due to:

- (1) Promotion of $3d$ -electrons of the central atom/ion to $4p$ -orbitals
(2) Promotion of $3d$ -electrons of the central atom/ion to $4s$ -orbitals
(3) Promotion of $3d$ -electrons of the central atom/ion within d -orbitals
(4) Promotion of $4s$ -electrons of the central atom/ion to $4p$ -orbitals

14. If a transition-metal compound absorbs violet-indigo radiation in the visible region. Its colour would be

- (1) Green
(2) Yellow
(3) Orange
(4) Blue

15. Transition metal compounds are usually coloured. This is due to the electronic transition:

- (1) From d -orbital to s -orbital
(2) From p -orbital to s -orbital
(3) From d -orbital to p -orbital
(4) Within the d -orbitals

16. Which of the following compound is not coloured?

- (1) $\text{Na}_2[\text{CuCl}_4]$ (2) $\text{Na}_2[\text{CdCl}_4]$
(3) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (4) $\text{K}_3[\text{Fe}(\text{CN})_6]$

17. The colour of Cu^+ compound is

- (1) White (2) Blue
(3) Orange (4) Yellow

Crystal Field Theory (CFT)

18. Which of the following complex has higher Δ_0 value?

- (1) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
(3) $[\text{Fe}(\text{CN})_6]^{3-}$ (4) All have equal

19. Relative to the average energy in the spherical crystal field, the t_{2g} orbitals in tetrahedral field is

- (1) Raised by $(2/5) \Delta_t$ (2) Lowered by $(2/5) \Delta_t$
(3) Raised by $(3/5) \Delta_t$ (4) Lowered by $(1/5) \Delta_t$

20. The crystal field splitting energy for octahedral (Δ_0) and tetrahedral (Δ_t) complexes is related as:

- (1) $\Delta_t = \frac{4}{9} \Delta_0$ (2) $\Delta_t = \frac{1}{2} \Delta_0$
(3) $\Delta_0 = -2\Delta_t$ (4) $\Delta_0 = -\frac{4}{9} \Delta_t$

21. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (atomic number of Cr = 24) has a magnetic moment of 3.83 BM. The correct distribution of $3d$ -electrons in the chromium present in the complex is

- (1) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{zx}$ (2) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{z^2}$
(3) $3d^1_{(x^2-y^2)}, 3d^1_{z^2}, 3d^1_{zx}$ (4) $3d^1_{xy}, 3d^1_{(x^2-y^2)}, 3d^1_{xz}$

22. In which of the following coordination entities, the magnitude of Δ_0 [CFSE in octahedral field] will be maximum?

- (1) $[\text{Co}(\text{CN})_6]^{3-}$ (2) $[\text{CoF}_6]^{3-}$
(3) $[\text{Co}(\text{NO}_2)_6]^{3-}$ (4) $[\text{Co}(\text{NH}_3)_6]^{3+}$

23. In which of the following configurations will there be the possibility of both para and diamagnetism, depending on the nature of the ligands?

- (1) d^3 (2) d^7
(3) d^6 (4) d^5

24. For Mn^{3+} ion, the electron pairing energy P is about $28,000 \text{ cm}^{-1}$, Δ_0 values for the complexes $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Mn}(\text{CN})_6]^{3-}$ are $15,800 \text{ cm}^{-1}$ and $38,500 \text{ cm}^{-1}$ respectively, which of the following complex is high spin:

- (1) Both are high spin (2) $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$
(3) $[\text{Mn}(\text{CN})_6]^{3-}$ (4) None of these

25. Which of the following ligands are correctly represented in an spectrochemical series?



126. The increasing order of the crystal field splitting power of some common ligands is

- (1) $\text{NH}_3 < \text{NO}_2^- < \text{CN}^- < \text{H}_2\text{O}$
(2) $\text{H}_2\text{O} < \text{NO}_2^- < \text{CN}^- < \text{NH}_3$
(3) $\text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2^- < \text{CN}^-$
(4) $\text{H}_2\text{O} < \text{NH}_3 < \text{CN}^- < \text{NO}_2^-$

127. The value of "spin only" magnetic moment for one of the following configuration is 2.84 BM. The correct one is

- (1) d^4 (in strong field ligand)
(2) d^2 (in weak field ligand)
(3) d^3 (in weak as well as in strong field ligand)
(4) d^5 (in strong field ligand)

128. The complex ion which has no d -electron in the central metal atom is

- (1) $[\text{MnO}_4]^-$ (2) $[\text{Co}(\text{NH}_3)_6]^{3+}$
(3) $[\text{Fe}(\text{CN})_6]^{3-}$ (4) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

129. Which of the following statements is correct for the complex $\text{Ca}_2[\text{Fe}(\text{CN})_5\text{O}_2]$ having t_{2g}^6, e_g^0 electronic configuration?

- (1) d^2sp^3 hybridised and diamagnetic
(2) sp^3d^2 hybridised and paramagnetic
(3) sp^3d^2 hybridised and diamagnetic
(4) d^2sp^3 hybridised and paramagnetic

130. Which of the following complex is inner orbital as well as low spin complex?

- (1) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (2) $[\text{Fe}(\text{CN})_6]^{3-}$
(3) $[\text{Cu}(\text{CN})_4]^{3-}$ (4) $[\text{Mn}(\text{NH}_3)_6]^{2+}$

131. The magnetic moment of a certain complex (A) of Co was found to be 4.89 BM and the EAN as 36. Co also forms complex (B) with magnetic moment 3.87 BM and EAN as 37, and complex (C) with EAN as 36 but diamagnetic. Which of the following statements is true regarding the above observation?

- (1) The oxidation states of Co in (A), (B) and (C) are +3, +2 and +3, respectively.
(2) Complexes (A) and (B) have sp^3d^2 hybridisation state while (C) has dsp^3 hybridisation state.
(3) The spin multiplicities of Co in (A), (B) and (C) are 3, 2 and 1, respectively.
(4) The oxidation states of Co in (A), (B) and (C) are +6, +8 and +1, respectively.

132. Spin only magnetic moments of a d^8 ion in octahedral, square planar, and tetrahedral complexes, respectively, are

- (1) 2.8 BM, 0 and 2.8 BM (2) 0, 0 and 0 BM
(3) 2.8, 2.8 and 2.8 BM (4) None of these

133. Given the following data about the absorption maxima of several complex ions, what is the order of Δ_0 for these ions?

Compound	λ_{max}
I. $[\text{CrCl}_6]^{3-}$	758
II. $[\text{Cr}(\text{NH}_3)_6]^{3+}$	465
III. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	694

- (1) $\Delta_0(\text{I}) < \Delta_0(\text{II}) < \Delta_0(\text{III})$
 (2) $\Delta_0(\text{II}) < \Delta_0(\text{III}) < \Delta_0(\text{I})$
 (3) $\Delta_0(\text{I}) < \Delta_0(\text{III}) < \Delta_0(\text{II})$
 (4) $\Delta_0(\text{III}) < \Delta_0(\text{II}) < \Delta_0(\text{I})$

134. Predict the order of Δ_0 for the following compounds:

- I. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ II. $[\text{Fe}(\text{CN})_2(\text{H}_2\text{O})_4]$
 III. $[\text{Fe}(\text{CN})_4(\text{H}_2\text{O})_2]^{2-}$
 (1) $\Delta_0(\text{I}) < \Delta_0(\text{II}) < \Delta_0(\text{III})$ (2) $\Delta_0(\text{II}) < \Delta_0(\text{I}) < \Delta_0(\text{III})$
 (3) $\Delta_0(\text{III}) < \Delta_0(\text{II}) < \Delta_0(\text{I})$ (4) $\Delta_0(\text{II}) < \Delta_0(\text{III}) < \Delta_0(\text{I})$

135. Among the following pairs of complexes, in which case the Δ_0 value is higher for the second compound.

- (1) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$
 (2) $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{CoCl}_6]^{3-}$
 (3) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
 (4) $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$

136. Which of the following complexes have high stability constant (k_s) value.

- (1) $[\text{PtBr}_4]^{2-}$ (2) $[\text{Pt}(\text{NH}_3)\text{Br}_3]^\ominus$
 (3) $[\text{Pt}(\text{NH}_3)_3\text{Br}]^\oplus$ (4) $[\text{Pt}(\text{NH}_3)_4]^{2+}$

137. The complex ion having minimum wavelength of absorption in the visible region is:

- (1) $\text{Cis-}[\text{CrBr}_2(\text{NH}_3)_4]^\oplus$ (2) $\text{Trans-}[\text{CrBr}_2(\text{NH}_3)_4]^\oplus$
 (3) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (4) $[\text{CrBr}(\text{NH}_3)_5]^{2+}$

138. Select the pairs having green and violet colour respectively.

- (1) (I) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_3$; (II) $[\text{Cr}(\text{H}_2\text{O})_4\text{Br}_2]\text{Br} \cdot 2\text{H}_2\text{O}$
 (2) (I) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_2$; (II) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_3$
 (3) (I) $[\text{Cr}(\text{ONO})(\text{H}_2\text{O})_5]\text{Br}_2$ (II) $[\text{Cr}(\text{NO}_2)(\text{H}_2\text{O})]\text{Cl}_2$
 (4) (I) $[\text{PrCl}(\text{NH}_3)_3]\text{NO}_2$; (II) $[\text{Pt}(\text{NO}_2)(\text{NH}_3)_3]\text{Cl}$

139. Select incorrect match between compound and reason for its observed colour.

- (1) HgI_2 : Polarization
 (2) Ag_2PO_4 : Polarization
 (3) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$: d-d transition
 (4) MnO_4^- : charge transfer spectrum.

140. If the colour of $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2]^{2+}$ (I) is blue-purple then what would be the colour of $[\text{Ni}(\text{en})_3]^{2+}$ (II)?

- (1) Violet (2) Deep blue
 (3) Pale blue (4) Green

141. Which of the following compounds absorbs at shorter wavelength in visible spectrum?

- (1) $[\text{CrBr}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ (2) $[\text{CrBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$
 (3) $[\text{CrBr}(\text{H}_2\text{O})_5]\text{Br}_2 \cdot \text{H}_2\text{O}$ (4) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_3$

142. CFSE value for brown ring complex for test of NO_3^- ion is

- (1) $-2.4 \Delta_0$ (2) $-1.8 \Delta_0$
 (3) $-0.8 \Delta_0$ (4) $-0.4 \Delta_0$

Application of Coordination Compounds and Miscellaneous

143. Which of the following is **incorrect** about Wilkinson's catalyst?

- (1) It is a diamagnetic complex.

- (2) It is a non-ionic complex.
 (3) It is a tetrahedral complex.
 (4) It is very effective for selective hydrogenation of organic molecule at room temperature and pressure.

144. Which bond properties are consistent with one another?

- | Bond order | Bond length | Vibrational frequency |
|------------|-------------|-----------------------|
| (1) higher | shorter | higher |
| (2) lower | shorter | lower |
| (3) higher | longer | lower |
| (4) lower | longer | higher |

145. Select the correct order of C—O bond order in mixed phosphine carbonyl complex:

- I. $[\text{Mo}(\text{Ph}_3\text{P})_3(\text{CO})_3]$ II. $[\text{Mo}(\text{Ph}_2\text{PCl})_3(\text{CO})_3]$
 III. $[\text{Mo}(\text{PhCl}_2)_3(\text{CO})_3]$

- (1) $\text{I} > \text{II} > \text{III}$ (2) $\text{I} < \text{II} < \text{III}$
 (3) $\text{I} = \text{II} > \text{III}$ (4) $\text{I} < \text{II} > \text{III}$

146. Compare C—C bond length (x) of C_2H_4 in Zeise's salt and C—C bond length (y) of $\text{C}_2(\text{CN})_4$ in $\text{K}[\text{PtCl}_3\text{C}_2(\text{CN})_4]$:

- (1) $x > y$ (2) $y > x$
 (3) $x = y$ (4) None of these

147. Which of the following organometallic compound is a σ and π -bonded?

- (1) $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$ (2) $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]$
 (3) $[\text{Co}(\text{CO})_5\text{NH}_3]^{2+}$ (4) $[\text{Fe}(\text{CH}_3)_3]$

148. Which of the following statement(s) is/are true or false?

S_1 : Complexes having d^0 or d^{10} configuration of metal ions are always diamagnetic.

S_2 : In organometallic compounds, carbon is bonded to metals directly.

S_3 : In $\text{Fe}(\text{CO})_5$, the Fe—C bond possesses both σ and π characteristics.

S_4 : Extra stability of metal carbonyls is explained by synergic bonding.

- (1) TTTT (2) FTFT
 (3) TTFF (4) FTTT

149. Which of the following complex can act as an oxidising agent as well as reducing agent?

- (1) $\text{Mn}(\text{CO})_5$ (2) $\text{Ti}(\text{CO})_6$
 (3) $\text{Mn}(\text{CO})_6$ (4) None of these

150. Which of the following statements is correct for the $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ complex?

- (1) The EAN value of Fe in this complex depends on the charge of NO ligand.
 (2) The EAN value of Fe in this complex does not depend on the charge of NO ligand.
 (3) The hybridisation of the central atom is d^2sp^3 .
 (4) It is paramagnetic with $\mu = 1.73 \text{ BM}$

151. Which of the following is not considered as an organometallic compound?

- (1) Ferrocene (2) Cis-platin
 (3) Zeise's salt (4) Grignard reagent

152. Among the following, which is not the π -bonded organometallic compound?

- (1) $(\text{CH}_3)_4\text{Pb}$ (2) $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$
 (3) $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$ (4) $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]$
153. Mg is an important component of which biomolecule occurring extensively in living world?
 (1) Haemoglobin (2) Chlorophyll
 (3) Florigen (4) ATP
154. What is the shape of $\text{Fe}(\text{CO})_5$ molecule and which of the following d -orbitals involved in hybridization?
 (1) Tetrahedral $d_{x^2-y^2}$
 (2) Trigonal bipyramidal, $d_{x^2-y^2}$
 (3) Trigonal bipyramidal, d_{z^2}
 (4) Square pyramidal
155. Among the properties (A) reducing, (B) oxidising, (C) complexing, the set of properties shown by CN^- ion towards metal species is
 (1) B, C (2) A, B, C
 (3) C, A (4) A, B
156. Ferrocene is
 (1) $[\text{Fe}(\eta^2\text{-C}_6\text{H}_5)_2]$ (2) $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$
 (3) $[\text{Fe}(\eta^6\text{-C}_6\text{H}_6)_2]$ (4) $[\text{Fe}(\eta^3\text{-C}_3\text{H}_3)_2]$
157. Dimethylglyoxime is coordinated to Ni^{2+} through:
 (1) Two oxygen atoms
 (2) Two nitrogen atoms
 (3) Two oxygen and one nitrogen atoms
 (4) Two oxygen and two nitrogen atoms
158. In isolated condition C—C bond length of C_2H_4 is x , than the bond length of C—C bond of C_2H_4 in Zeise's salt is
 (1) Greater than x (2) Less than x
 (3) Equal to x (4) None of these
159. When $\text{K}_4[\text{Fe}(\text{CN})_6]$ is treated with FeCl_3 , a blue colour is obtained. It is due to the formation of
 (1) $\text{Fe}^{II}[\text{Fe}^{III}(\text{CN})_6]^\ominus$ (2) $\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_6]^\ominus$
 (3) Both (a) and (b) (4) None of these
160. The common features among the species CN^- , CO and NO^+ are
 (1) bond order three and isoelectronic
 (2) bond order three and weak field ligands
 (3) isoelectronic and weak field ligands
 (4) bond order two and π -acceptors
161. Consider the following complex:
 $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{BrO}$
 the coordination number, oxidation number, number of d -electrons and number of unpaired d -electrons of the metal are respectively:
 (1) 6, 3, 6, 0 (2) 7, 1, 6, 4
 (3) 7, 2, 7, 1 (4) 6, 2, 7, 3
162. The bond length of C—O bond in carbon monoxide is 1.128 Å. The C—O bond in $[\text{Fe}(\text{CO})_5]$ is
 (1) 1.115 Å (2) 1.128 Å
 (3) 1.178 Å (4) 1.150 Å

163. The most stable ion is

- (1) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ (2) $[\text{Fe}(\text{Cl})_6]^{3-}$
 (3) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (4) $[\text{Fe}(\text{SCN})_6]^{3-}$

 164. The number of σ and π -bonds in $\text{Fe}_2(\text{CO})_9$, respectively, are

- (1) 22 σ and 15 π (2) 22 σ and 16 π
 (3) 23 σ and 15 π (4) 15 σ and 8 π

 165. Ag^+ forms many complexes, some of these are $[\text{Ag}(\text{NH}_3)_2]^+$, $2[\text{Ag}(\text{CN})_2]^\ominus$, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$.

Which of the following statements is true?

- (1) In these complexes, Ag^+ is a Lewis base
 (2) The hybridisation of Ag^+ is sp^2 .
 (3) The Ag^+ complexes are good reducing agents
 (4) These complexes are all linear

166. Hardness of water is estimated by simple complex formation titration. Complex formed by cation in hard water during estimation of hardness is

- (1) $\text{Na}_2[\text{Ca}(\text{PO}_3)_6]$ (2) $\text{Na}_2[\text{Mg}(\text{EDTA})]$
 (3) $[\text{Ca}(\text{SO}_4)_2]^{2-}$ (4) $\text{Na}_2[\text{Pb}(\text{EDTA})]$

 167. The ligand called π -acid is

- (1) CO (2) $\text{C}_2\text{O}_4^{2-}$
 (3) NH_3 (4) ethylene

168. The complex used as an anticancer agent is

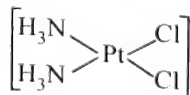
- (1) $\text{mer-}[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (2) $\text{cis-}[\text{PtCl}_2(\text{NH}_3)_2]$
 (3) $\text{Na}_2[\text{CoCl}_4]$ (4) $\text{cis-K}_2[\text{Pt}(\text{Cl}_2\text{Br}_2)]$

169. Which is used in cancer chemotherapy?

- (1) cis-platin (2) Zeise's salt
 (3) Both (a) and (b) (4) None of these

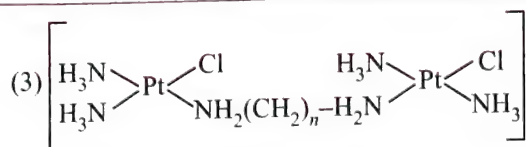
170. Zeise's salt is

- (1) $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$
 (2) $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$
 (3) $\text{K}[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_3]$
 (4) $\text{K}[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)_2\text{Cl}_2]$

 171. cis-diamminedichloridoplatinum(II), $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, is


One of the number of platinum coordination compound is used in the treatment of cancer. Commonly known as **cis-platin**, this compound has the ability to block the uncontrolled division of cancerous cells that results in the growth of tumours. Recent studies show that cisplatin can cause serious side effects, including severe kidney damage. cis-platin is replaced by which of the following compounds:

- (1) $\begin{bmatrix} \text{Cl} & & \text{NH}_3 \\ & \text{Pt} & \\ \text{H}_3\text{N} & & \text{NH}_2(\text{CH}_2)_n\text{NH}_2 \end{bmatrix} \begin{bmatrix} \text{H}_3\text{N} & & \text{Cl} \\ & \text{Pt} & \\ & & \text{NH}_3 \end{bmatrix}$
 trans-isomer ($n = 2$ to 6)
- (2) $\begin{bmatrix} \text{H}_3\text{N} & & \text{Cl} \\ & \text{Pt} & \\ \text{H}_3\text{N} & & \text{NH}_2(\text{CH}_2)_n\text{NH}_2 \end{bmatrix} \begin{bmatrix} \text{Cl} & & \text{NH}_3 \\ & \text{Pt} & \\ & & \text{NH}_3 \end{bmatrix}$
 ($n = 2$ to 6)



(4) None of the above is correct.

172. Select the incorrect statement about metal carbonyls?

- (1) Metal acts as Lewis base as well as Lewis acid
- (2) CO acts as Lewis base as well as Lewis acid
- (3) $p\pi-p\pi$ back bonding takes place
- (4) $p\pi-d\pi$ back bonding takes place

173. The following metal carbonyls are given:

- (I) $[\text{Mn}(\text{CO})_6]^{\oplus}$
- (II) $[\text{Cr}(\text{CO})_6]$
- (III) $[\text{V}(\text{CO})_6]^{\ominus}$

Which of the following is correct order of CO bond strength in the above complexes

- (1) $\text{I} > \text{II} > \text{III}$
- (2) $\text{III} > \text{II} > \text{I}$
- (3) $\text{II} > \text{I} > \text{III}$
- (4) $\text{III} > \text{I} > \text{II}$

174. The following compounds are given:

- (I) $[\text{Mn}(\text{CO})]^\ominus$
- (II) CO
- (III) $\text{OC} \rightarrow \text{BH}_3$
- (IV) $[\text{Fe}(\text{CO})_5]$

Select the correct CO bond order in the given compounds

- (1) $\text{IV} > \text{III} > \text{I} > \text{II}$
- (2) $\text{I} > \text{IV} > \text{III} > \text{II}$
- (3) $\text{II} > \text{I} > \text{IV} > \text{III}$
- (4) $\text{III} > \text{II} > \text{IV} > \text{I}$

175. The π -acid ligand which uses its d -orbital during synergic bonding in its complex compound is:

- (1) PR_3
- (2) CO
- (3) C_6H_6
- (4) NO^\oplus

176. Which of the following ligand does not act as π -acid ligand?

- (1) O_2^{2-}
- (2) C_2H_4
- (3) N_2
- (4) CO

177. Select the correct statement about the above given compound

- (1) 'C—O' bond is weakest in cation and strongest in anion.
- (2) 'C—O' bond is strongest in cation and weakest in anion.
- (3) 'C—O' bond is longer in cation than in the anion.
- (4) ('M—C') π -bonding is higher in the cation

178. The π -acid ligand which uses its d -orbital during synergic bonding in its complex compound.

- (1) NO
- (2) N_2
- (3) PR_3
- (4) CN^\ominus

Jahn-Teller Distortion

179. Which of the following configuration is more stable for the $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

- (1) $t_{2g}^6 (d_{z^2})^2 (d_{x^2-y^2})^1$
- (2) $t_{2g}^6 (d_{z^2})^1 (d_{x^2-y^2})^2$
- (3) $t_{2g}^5 (d_{z^2})^2 (d_{x^2-y^2})^2$
- (4) All

180. Which of the following configuration high spin octahedral complexes shown strong distortion.

- (I) $t_{2g}^3 e_g^1$
- (II) $t_{2g}^3 e_g^3$
- (III) $t_{2g}^0 e_g^0$
- (IV) $t_{2g}^1 e_g^0$

(1) I, II

(3) II, III

(2) I, II, III

(4) I, III, IV

181. Slow spin octahedral complexes show strong distortion.

- (I) $t_{2g}^1 e_g^0$
- (II) $t_{2g}^3 e_g^0$
- (III) $t_{2g}^6 e_g^1$
- (IV) $t_{2g}^6 e_g^3$
- (1) I, II
- (2) I, II, III
- (3) III, IV
- (4) I, III, IV

182. Which of the following configuration in either high spin or low spin complexes show no distortion.

- (I) $t_{2g}^3 e_g^2$
- (II) $t_{2g}^6 e_g^2$
- (III) $t_{2g}^3 e_g^0$
- (IV) $t_{2g}^6 e_g^1$
- (1) I, II
- (2) II, III
- (3) I, II, III
- (4) All

183. Which of the following statement is/are correct.

- (I) Cl^- has greater trans effect than NH_3 .
- (II) Trans effect is used in the synthesis of cisplatin (cis-isomer) and its trans isomer starting from PtCl_4^{2-} .
- (III) Starting from $[\text{Pt}(\text{NH}_3)_4]^{2+}$, the synthesis of cisplatin (cis-isomer) is obtained exclusively.
- (IV) CH_3^- has greater trans effect than H^- .
- (1) I, II
- (2) II, III
- (3) III, IV
- (4) I, III

Multiple Correct Answers Type

Naming, Terminology and Ligands

1. Select the correct statement(s) for double salt.

- (1) Double salts are stable in solid state but lose their identity in aqueous solution.
- (2) In double salt the properties of constituent ions are not changed in their aqueous solution.
- (3) Double salts are stable in solid state and do not lose their identity in aqueous solution.
- (4) In double salt the properties of constituent ions are changed in their aqueous solution.

2. Which of the following ligand(s) is/are ambidentate?

- (1) NOS^\ominus
- (2) SCN^\ominus
- (3) NO_2^\ominus
- (4) $\text{CH}_3\text{COO}^\ominus$

3. Select the correct IUPAC name for $[\text{CoCl}_2(\text{en})_2](\text{ClO}_3)_2$.

- (1) Dichloridobis (ethylenediamine)cobalt(III) chlorate
- (2) Dichloridobis (ethane-1, 2-diamine)cobalt(III) chlorate
- (3) bis {dichloridoethylenediaminecobalt(III)} chlorate
- (4) bis {di(chlorido)ethylenediaminecobalt(III)} chlorate

4. Bidentate ligands are

- (1) $\text{C}_2\text{O}_4^{2-}$ (oxalate)
- (2) en (ethylenediamine)
- (3) DMG (dimethyl glyoxime)
- (4) Gly (glycine)

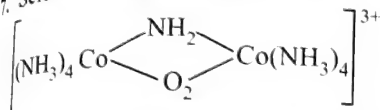
5. Which of the following complex(s) is/are having correct name?

- (1) $\text{Cs}[\text{Pt}(\text{NH}_3)_5\text{I}]$ Cesium amminepentaiodidoplatinate(IV)
 (2) $[\text{Ag}(\text{CN})_2]^\ominus$ Dicyanidoargentate(I) ion
 (3) $\text{Rb}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ Rubidium trioxalatochromate(III)
 (4) $\text{K}_2[\text{Ni}(\text{EDTA})]$ Potassium ethylenediaminetetraacetatoni-
 ckel(II)

6. Which can form chelates?

- (1) Ethylene diamine (2) Oxalate
 (3) Glycinate (4) Cyanide

7. Select the correct IUPAC name for the following:



- (1) Tetramminecobalt (III)- μ -amido- μ -peroxidotetraamminecobalt (III) ion
 (2) μ -Amido- μ -peroxidobis(tetraammine)dichalcobalt-(III) ion
 (3) μ -Amido- μ -peroxidobis(tetraamminecobalt(III)) ion
 (4) μ -Amido- μ -peroxidoctaamminecobalt(III) ion

8. Which of the following statement(s) is/are correct?

- (1) Primary valency of the central metal of a complex is always satisfied by anions.
 (2) Secondary valency of the central metal of a complex may be satisfied by either negative ions or neutral molecules.
 (3) Species which show primary valencies in a complex compound can be precipitated out.
 (4) None of these

9. Which of the following complex(s) is/are an example of homoleptic complex?

- (1) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (2) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
 (3) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ (4) $[\text{Ni}(\text{NH}_3)_4\text{Cl}_2]$

10. Which of the following ligand(s) can act as π -acid ligand?

- (1) $\text{B}_3\text{N}_3\text{H}_6$ (2) π -cyclopentadienyl
 (3) π -Allyl (4) σ -cyclopentadienyl

Isomerism

11. Which of the following molecule(s) is/are **not** showing optical isomerism?

- (1) $[\text{Co}(\text{NH}_3)_3\text{I}]^\oplus$ (2) $[\text{Co}(\text{en})(\text{NH}_3)_2]^{2+}$
 (3) $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$ (4) $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$

12. Which of the following complex ion(s) is/are **not** expected to absorb visible light?

- (1) $[\text{Ti}(\text{en})_2(\text{NH}_3)_2]^{4+}$ (2) $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 (3) $[\text{Zn}(\text{NH}_3)_6]^{2+}$ (4) $[\text{Sc}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{3+}$

13. The complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ is formed in the brown ring test for nitrates when freshly prepared FeSO_4 solution is added to aqueous solution of NO_3^- followed by addition of conc. H_2SO_4 . Select correct statements about this complex:

- (1) Colour change is due to charge transfer.
 (2) It has iron in +1 oxidation state and nitrosyl as NO^\oplus .
 (3) It has magnetic moment of 3.87 BM confirming three unpaired electrons in Fe.
 (4) In complex Fe has d^2sp^3 hybridisation.

14. Which of the following represent the correct sequence of indicated property?

- (1) $\text{Mn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+}$: magnetic moment
 (2) $\text{FeO} > \text{CoO} > \text{NiO}$: basic character
 (3) $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$: number of oxidation states
 (4) 1.73μ : one unpaired electron

15. Which of the following complexes are diamagnetic?

- (1) $[\text{AuI}_4]^\ominus$ (2) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 (3) $[\text{CoI}_6]^{3-}$ (4) $[\text{Co}(\text{CO})_4]^\ominus$

16. Which of the following molecule(s) is/are showing optical isomerism?

- (1) $[\text{Co}(\text{NH}_3)_3\text{Br}_3]$ (2) $[\text{Co}(\text{en})\text{Br}_2(\text{NH}_3)_2]^\oplus$
 (3) $[\text{Co}(\text{en})_3]^{3+}$ (4) $[\text{Co}(\text{en})_2\text{Br}_2]^\oplus$

17. Both geometrical and optical isomerisms **are not shown by**

- (1) dibromidobis (ethylenediamine) cobalt(III) ion
 (2) tetraamminedibromido cobalt(III) ion
 (3) tetraamminedibromido cobalt(III) ion
 (4) trioxalatochromate(III) ion

18. Which of the following statement(s) is/are correct?

- (1) The complexes $[\text{NiI}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ differ in state of hybridisation of nickel.
 (2) The complexes $[\text{NiI}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ differ in geometry.
 (3) The complexes $[\text{NiI}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ differ in the magnetic properties.
 (4) The complexes $[\text{NiI}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ differ in primary valencies of nickel.

19. In which case geometrical isomer *cis* is possible with M as metal ion if complexes are square planar having CN = 4?

- (1) MX_2Y_2 (2) MX_2YZ
 (3) MXY_2Z (4) MX_4

20. $d_{x^2-y^2}$ orbital is involved in which of the following hybridisation?

- (1) sp^3d^3 (2) dsp^2
 (3) sp^3d^2 (4) sp^3d

21. Which complex species does/do not exhibit geometrical isomerism and only have two stereoisomerism?

- (1) $[\text{PtBrI}(\text{gly})]^\ominus$ (2) $[\text{Cr}(\text{EDTA})]^\ominus$
 (3) $[\text{Cr}(\text{acac})_2(\text{en})]^\oplus$ (4) $[\text{Pd}(\text{CN})(\text{OX})(\text{gly})]$

22. Which of the following complex(s) cannot exhibit both geometrical and optical isomerism?

- (1) $[\text{Co}(\text{H}_2\text{O})\text{Br}_3]$ (2) $[\text{Pt Br Cl FI}]^{2-}$
 (3) $[\text{Fe Cl}_2(\text{en})_2]^\oplus$ (4) $[\text{Ru}(\text{en})_3]^{+3}$

23. Select the correct statement about the complex $[\text{Cr Br}(\text{CN})(\text{en})_2]^\oplus$?

- (1) It has three optically active isomers: *d*, *l* and *trans* form
 (2) Only the *cis* isomer shows optical activity
 (3) It shows two geometrical isomers *cis* and *trans*.
 (4) *Cis* and *trans* forms are not diastereomers to each other

24. Which of the following statement(s) is/are correct?

- (1) IUPAC name of $\text{Ca}[\text{Cr}(\text{CN})_2\text{O}_2(\text{O}_2)(\text{H}_2\text{O})]$ is calcium aquadicyanoperoxosuper oxo chromate (III)
- (2) $[\text{Cr Cl I}(\text{en})_2]^{\oplus}$ shows optical isomerism
- (3) $[\text{Pt abcd}]^{n\pm}$ type and $[\text{Pt abcd}]^{n\pm}$ type compounds shows 3 geometrical and 30 stereoisomer's respectively
- (4) Cis and trans forms are diastereomers to each other

25. Which of the following statement is correct for the complex $[\text{CrBr}_3(\text{OH})_2(\text{NH}_3)]^{2-}$ ion?

- (1) It has three geometrical isomers
- (2) It shows four stereoisomer's
- (3) Only one stereoisomer is optically active and remaining are inactive
- (4) The complex have three unpaired e^- 's

26. In the test for NO_3^- ion, the dark brown ring complex is formed, which statement(s) is/are correct of this complex.

- (1) Fe and No both have +1 charge
- (2) The colour is due to charge transfer spectra.
- (3) Fe has +2 oxidation state and NO is neutral
- (4) The complex can be represented as $[\text{Fe}(\text{H}_2\text{O})_4\text{NO}]^{+2}$

27. In an aqueous solution of NiBr_2 , if (en) is progressively added in molar ratios such as $\text{Ni} : \text{en} :: 1:1, 1:2, 1:3$ then three octahedron complexes x, y, z formed respectively. Select the correct statement(s) about x, y and z.

- (1) Complex x has maximum value of absorbed wavelength
- (2) Complex y is coloured
- (3) Complex z has maximum number of chelates
- (4) All three are paramagnetic outer orbital complexes

28. Which of the following pair of complex compound(s) has/ have different colour?

- (1) d and l form of $[\text{Ni}(\text{en})_3]^{2+}$
- (2) cis and trans form of $[\text{IrCl}_2(\text{en})_2]\text{Br}$
- (3) $[\text{Cr}(\text{NO}_2)_2(\text{NH}_3)_4]^{\oplus}$ and $[\text{Cr}(\text{ONO})_2(\text{NH}_3)_4]^{\oplus}$
- (4) $[\text{CrCl}(\text{NO}_2)(\text{NH}_3)_4]\text{Cl}$ and $[\text{CrCl}_2(\text{NH}_3)_4]\text{NO}_2$

29. The complex $[\text{Ni}(\text{PPh}_3)_2(\text{CNS})_2]$ is paramagnetic. The analogous complex of Pd^{+2} is diamagnetic. The isomerism shown by Pd^{+2} complex is/are:

- (1) Polymerisation
- (2) Linkage
- (3) Optical
- (4) Geometrical

30. Which of the following complex ion(s)/compounds shows geometrical isomerism but none of them shows optical isomerism?

- (1) $[\text{CoCl}_4(\text{en})]^-$
- (2) $[\text{Pt Br I}(\text{H}_2\text{O})(\text{NH}_3)]$
- (3) $[\text{Cr}(\text{en})_3]^{3+}$
- (4) $[\text{CrCl}_3(\text{H}_2\text{O})_2(\text{NH}_3)]$

31. In which of the following compounds d-orbitals lose their degeneracy?

- (1) Anhydrous CuSO_4
- (2) $\text{K}_3[\text{Fe}(\text{CN})_6]$
- (3) $\text{K}_4[\text{Fe}(\text{CN})_6]$
- (4) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Hybridisation, VBT, CFT

32. A d-block element forms octahedral complex, but its spin magnetic moment remains same either in strong field or in weak field ligand. Which of the following is /are correct?

- (1) Element always forms colourless compound.
- (2) Number of electrons in t_{2g} orbitals are higher than in e_g orbitals.
- (3) It can have either d^3 or d^8 configuration.
- (4) It can have either d^7 or d^8 configuration.

33. Which of the following is/are characteristic of a tetrahedral complex?

- (1) $d_{x^2-y^2}$ and d_{z^2} orbitals are low energy orbitals.
- (2) Most tetrahedral complexes are high spin.
- (3) Crystal field splitting is found double in octahedral complexes.
- (4) Splitting pattern in tetrahedral complex is just opposite of that in octahedral complexes.

34. The complex $\text{K}_4[\text{Zn}(\text{CN})_4(\text{O}_2)_2]$ is oxidised into $\text{K}_2[\text{Zn}(\text{CN})_4(\text{O}_2)_2]$, then which of the following is/are correct:

- (1) Zn(II) is oxidised in to Zn(IV)
- (2) Paramagnetic moment decreases
- (3) O—O bond length decreases
- (4) Paramagnetic moment increases

35. Select the correct statement:

- (1) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is Co(III), low spin. 0 unpaired electron. diamagnetic
- (2) $[\text{CoF}_6]^{3-}$ is Co(III), high spin d^6 , 4 unpaired electron. paramagnetic
- (3) $[\text{RhF}_6]^{3-}$ is Rh(III), low spin d^6 , 0 unpaired electrons diamagnetic
- (4) $[\text{Fe}(\text{CN})_6]^{4-}$ is high spin d^6 , 0 unpaired electron diamagnetic

36. $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ complex is

- (1) High spin complex
- (2) Having d^2sp^3 -hybridization
- (3) Low spin complex
- (4) Having octahedral structure

37. Colourless, tetrahedral complexes among the following are

- (1) $\text{K}_3[\text{Cu}(\text{CN})_4]$
- (2) $\text{Ca}[\text{NiCl}_4]$
- (3) $\text{Na}[\text{BF}_4]$
- (4) $\text{Ni}(\text{CO})_4$

38. In which of the following complex ion five atoms are lying in a line including metal?

- (1) $[\text{Ag}(\text{CN})_2]^-$
- (2) $[\text{Pt}(\text{CN})_4]^{2-}$
- (3) $[\text{Ag}(\text{SCN})_2]^-$
- (4) $[\text{Zn}(\text{CN})_4]^{2-}$

39. Select the correct statement(s) for given carbonyl compounds:

- (1) "CO" bond order is lesser in $[\text{Nb}(\text{CO})_6]^-$ Then in $[\text{Tc}(\text{CO})_6]^{\oplus}$
- (2) "Nb—C" bond order in $[\text{Nb}(\text{CO})_6]^-$ is greater than "Tc—C" bond order in $[\text{Tc}(\text{CO})_6]^{\oplus}$
- (3) $[\text{Tc}(\text{CO})_6]^{\oplus}$ acts as reducing agent and $[\text{Nb}(\text{CO})_6]^-$ acts as oxidising agent.
- (4) $[\text{Nb}(\text{CO})_6]^-$ acts as reducing agent and $[\text{Tc}(\text{CO})_6]^{\oplus}$ acts as oxidising agent.

40. Select the correct statement(s):

- (1) In dsp^2 hybridisation, d_{z^2} orbital of central metal atom/ion is used.
- (2) Facial and meridional isomers associated with $[Ma^3b^3]^{n\pm}$ type complex compounds, both are optically inactive.
- (3) In metal carbonyl C—O increases compared to that CO molecule.
- (4) Chelation effect is maximum for five and six membered rings.

41. Select the correct statements:

- (1) Compounds $[Cr(H_2O)_6]Br_3$ and $[CrBr_3(H_2O)_3] \cdot 3H_2O$ are hydrate isomers.
- (2) Greater the charge on the central metal cation, greater the value of $\Delta(CFSE)$
- (3) $[CrBr_2(NH_3)_2(en)]^{\oplus}$ complex ion will have four different isomers.
- (4) In the complex ion $[CoF_6]^{3-}$, F^{\ominus} is a weak ligand, so that $\Delta_0 < P$ and it is low spin complex.

42. Select the correct statement(s):

- (1) $Ni(CO)_4$ is low spin complex
- (2) $[FeF_6]^{3-}$ is high spin complex
- (3) Strong ligand like CN^{\ominus} and NO_2^{\ominus} generally form low spin complexes.
- (4) Weak ligands F^{\ominus} , Cl^{\ominus} and OH^{\ominus} usually form high spin complexes.

43. Select the correct statement(s): for octahedral complexes:

- (1) In octahedral complexes, its magnetic moment remains same either in strong field or in weak field ligand in d^9 configuration.
- (2) Number of e^- 's in t_{2g} orbitals are higher than in e_g orbitals.
- (3) d^3 and d^8 configuration cannot exist in both high spin and low spin forms.
- (4) Chelating ligands are at least bidentate ligands.

44. Select the correct stability order for the following complexes.

- (1) $[Cu(trien)]^{2+} > [Cu(en)_2]^{2+} > [Cu(NH_3)_4]^{2+}$
- (2) $[Ir(H_2O)_6]^{3+} > [Rh(H_2O)_6]^{3+} > [Co(H_2O)_6]^{3+}$
- (3) $[Cr(NH_3)_6]^{3+} > [Cr(NH_3)_6]^{2+} > [Cr(NH_3)_6]^{\oplus}$
- (4) $[Fe(NH_3)_6]^{3+} > [Fe(NO_2)_6]^{3-} > [Fe(H_2O)_6]^{3+}$

45. Select the correct statement(s):

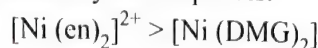
- (1) Order of energies of d -orbitals of metal ion in a square planar complex is:
 $d_x^2 - y^2 > d_{xy} > d_z^2 > d_{zx} = d_{yz}$
- (2) The CFSE of $[Co(NH_3)_6]Br_3$ is $-2.4\Delta_0$.
- (3) The magnitude of CFSE in octahedral field depends on nature of the ligand.
- (4) When NH_3 is added to $[Ni(H_2O)_6]^{2+}$, its magnetic moment does not change.

46. Select the correct statement(s)

- (1) Stability order of complexes is
 $[Cr(ox)_3]^{3-} > [Cr(H_2O)_6]^{3+} > [Co(ONO)_6]^{3-} > [CoF_6]^{3-}$
- (2) Among d^4 , d^5 , d^6 and d^7 configuration for an octahedral complexes, the maximum CFSE is given by low spin with d^5 configuration.

(3) In an octahedral field, the t_{2g} orbitals are raised in energy by $0.4\Delta_0$.

(4) Stability of complex is:



Application of Coordination Compounds

47. The coordination number of a central metal atom in a complex(s) is/are not determined by:

- (1) The number of only anionic ligands bonded to the metal ion.
- (2) The number of ligands around metal ion bonded by π -bonds.
- (3) The number of ligands around a metal ion bonded by both π and σ -bonds.
- (4) The number of ligands around a metal ion bonded by σ -bonds.

48. Which of the following statement(s) is/are incorrect?

- (1) Metal carbonyls are the examples of only σ -bonded organometallic complexes.
- (2) Metal carbonyls are the examples of only π -bonded organometallic complexes.
- (3) Metal carbonyls are the examples of organometallic complexes which involve both σ and π -bonds between metal and carbon of the carbonyl group.
- (4) Metal carbonyls involve both σ - and π -bonds between metal and oxygen of the carbonyl group.

49. Which of the following is an example of π -bonded organometallic complex?

- (1) Ferrocene
- (2) Dibenzenechromium
- (3) $Zn(C_2H_5)_2$
- (4) $Pb(C_2H_5)_4$

50. Which of the following is/are example(s) of σ -bonded organometallic compound?

- (1) $Al_2(CH_3)_6$
- (2) $Pb(CH_3)_4$
- (3) $Zn(C_2H_5)_2$
- (4) Ferrocene

51. Which of the following statement is correct regarding metal carbonyl?

- (1) In $Mn_2(CO)_{10}$, bond order of Mn—Mn is 0.
- (2) In $Fe_2(CO)_9$, number of Fe—Fe bonds is 1.
- (3) In $Ni(CO)_4$, all bond length are same.
- (4) $Fe(CO)_5$ is diamagnetic.

52. Select correct statements:

- (1) $[Ni(en)_3]^{2+}$ is less stable than $[Ni(NH_3)_6]^{2+}$.
- (2) Increase in stability of the complexes due to the presence of multidentate cyclic ligand is called macro-cyclic effect.
- (3) $[Ni(en)_3]^{2+}$ is more stable than $[Ni(NH_3)_6]^{2+}$.
- (4) For a given ion and ligand, the greater the charge on the metal ion, the greater is the stability.

53. In which of the following cases, the synergic bonding takes place at the π -orbital of the ligand?

- (1) $[PtCl_3(C_2H_4)]^{\ominus}$
- (2) $[Ni(PF_3)_4]$
- (3) $Cr(C_6H_6)_2$
- (4) $[Fe(\pi-C_5H_5)_2]$

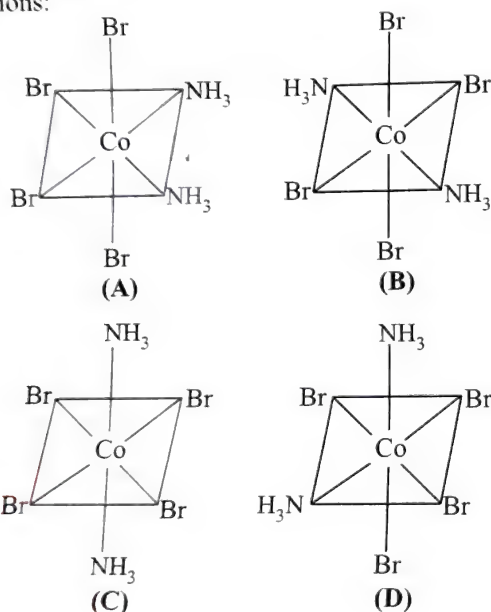
54. Which of the following statement(s) is/are correct?

- (1) The stability constant of $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is larger than that of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.
- (2) The cyano complexes are more stable than those formed by halide ions.
- (3) The stability of halide complexes follows the order $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$.
- (4) The stability constant of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is less than that of $[\text{CuCl}_4]^{2-}$.

Linked Comprehension Type

Paragraph 1

Consider the following isomers of $[\text{Co}(\text{NH}_3)_2\text{Br}_4]^\ominus$ and answer the questions:



1. Select the correct statement:

- (1) Pairs of A and D are same and pairs of B and C are also same.
- (2) All have chiral centres.
- (3) A and C are enantiomers.
- (4) B and D are enantiomers.

2. Out of these isomers:

- (1) A and D are trans and B and C are cis
- (2) A and D are cis and B and C are trans
- (3) A and B are cis and C and D are trans
- (4) A and B are trans and C and D are cis

3. In the complex $[\text{Zn PQRS}]^{2+}$:

- (1) There is chirality
- (2) There is geometrical isomerism
- (3) Both (a) and (b)
- (4) None of these

4. If PQRS are four different ligands, then how many geometric isomers will be found for square planar $[\text{Pt PQRS}]^{2+}$?

- (1) 1
- (2) 2
- (3) 3
- (4) 4

Paragraph 2

Ligands are broadly classified into two types, classical and non-classical ligands depending on their donor and acceptor ability. Classical ligands form classical complexes while non-classical ligands form non-classical complexes. Bonding mechanism in non-classical is called synergic bonding.

5. In compound $[\text{M}(\text{Co})_n]^z$, the correct match for highest 'M-C' bond length for given M, n and z respectively.

	M	n	z
(1)	Ti	6	-2
(2)	Mn	6	+1
(3)	Cr	6	0
(4)	V	6	-1

6. Synergic bonding is absent in:

- (1) $[\text{Ni}(\text{CN})_4]^{4-}$
- (2) $[\text{Cr}(\text{CO})_3(\text{B}_3\text{N}_3\text{H}_6)]$
- (3) $[\text{Mo}(\text{Co})_6]$
- (4) $[\text{Sc}(\text{Co})_6]^{3+}$

7. Which is not π -acceptor ligand?

- (1) $\sigma\text{-C}_5\text{H}_5$
- (2) PH_3
- (3)
- (4) $\text{B}_3\text{N}_3\text{H}_6$

Paragraph 3

Bond lengths and vibrational spectra are the two important physical evidences supporting the synergic bonding in non-classical complexes. Vibrational spectra is based on the fact that the compression and extension of a bond may be analogous to the behaviour of a spring and obeys Hook's law:

8. In $[\text{Mn}_2(\text{CO})_{10}]$ carbonyl complex, which d-orbitals of Mn-atom is not involved in synergic bonding between Mn and CO ligand.

- (1) d_{xy}
- (2) d_{yz}
- (3) d_{zx}
- (4) None of these.

9. In which of the following complex stretching frequency for CO ligand is least and bond energy of 'M-C' bond is highest.

- (1) $[\text{Mo}(\text{CO})_3(\text{PR}_3)_3]$
- (2) $[\text{Mo}(\text{CO})_3(\text{dien})]$
- (3) $[\text{Mo}(\text{CO})_3(\text{PF}_3)_3]$
- (4) $[\text{Mo}(\text{CO})_3(\text{PCl}_3)_3]$

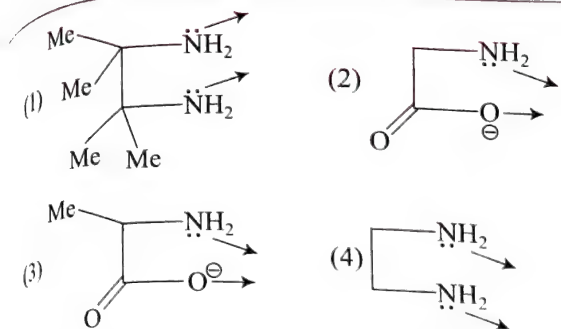
10. In which of the following ligand, σ -bond strength does not change during synergic bonding in their respective complexes.

- (1) $\text{P}(\text{C}_2\text{H}_5)_3$
- (2) N_2
- (3) $\text{CH}_2=\text{CH}_2$
- (4) CO

Paragraph 4

VBT and CFT play very important role in determining the geometry of complex compound/ion and electronic distribution of d-orbitals of central metal atom/ion in presence of given ligands respectively. A very important property of complex compound/ion is to display isomerism.

11. Which of the ligand can show geometrical as well as optical isomerism in square planar homoleptic complex?



12. Which of the following complex compound(s) is/are inner orbital complex as well as low spin complex ion(s)?

- (1) $[\text{Ni}(\text{CN})_6]^{4-}$ (2) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$
 (3) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (4) $[\text{IrF}_6]^{3-}$

13. Which of the following compound(s) shows at least two types of structural isomerism.

- (1) $\text{Na}[\text{Fe}(\text{CN})_2(\text{H}_2\text{O})_4]$ (2) $[\text{Co}(\text{SCN})(\text{H}_2\text{O})_5]\text{Cl}_2$
 (3) $[\text{PdCl}(\text{NO}_2)(\text{NH}_3)_4]\text{SO}_4$ (4) $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$

14. In which of the following complex transition of electron occurs from one shell to other shell of central metal.

- (1) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Ni}(\text{CN})_6]^{4-}$
 (3) $[\text{Rh}(\text{NH}_3)_6]^{2+}$ (4) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$

15. Which of following hydrated complex ion has high intensity colour in aqueous solution.

- (1) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$
 (3) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (4) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

Paragraph 5

Valence bond theory describes the bonding in complexes in terms of coordinate-covalent bonds resulting from overlap filled ligand orbitals with vacant metal hybrid orbitals. This theory explains magnetic behaviour and geometrical shape of coordination compounds. Magnetic moment of a complex, compound can be determined experimentally and theoretically by using spin only formula.

Magnetic moment $\sqrt{n(n+2)}$ BM (where n = No. unpaired electrons).

16. The value of spin only magnetic moment for octahedral complex of the following configuration is 2.84 BM. The correct statement is

- (1) d^4 (in weak field ligand)
 (2) d^2 (in weak field and in strong field ligand)
 (3) d^3 (in weak field and in strong field ligand)
 (4) d^5 (in strong field ligand)

17. Ni^{2+} cation combines with a uninegative monodentate ligand X^- to form a paramagnetic complex $[\text{NiCl}_4]^{2-}$. The number of unpaired electron(s) in central metal cation and geometry of this complex respectively are

- (1) One, tetrahedral (2) Two, tetrahedral
 (3) One, square planar (4) Two, square planar

Paragraph 6

Square planar complexes are formed by d^8 ions with strong field ligands. The crystal field splitting Δ_0 is larger for the second and

third row transition elements and for more highly charged species. All the complexes having $4d^8$ and $5d^8$ configurations are mostly square planar including those with weak field ligands such as halide ions. Square planar complexes can show geometrical isomerism but they do not show optical isomerism due to the presence of plane of symmetry.

18. Which of the following molecule has synergic bonding?

- (1) $[\text{Fe}(\pi\text{-C}_5\text{H}_5)_2]$ (2) $[\text{RhCl}(\text{PPh}_3)_3]^{3+}$
 (3) $[\text{Fe}(\text{Phen})_3]^{3+}$
 (4) All are having synergic bonding

19. Among the following complexes, which has a square planar geometry?

- (1) $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ (2) $\text{K}_3[\text{Cu}(\text{CN})_4]$
 (3) $[\text{Ni}(\text{CO})_4]$ (4) $\text{K}_2[\text{Zn}(\text{CN})_4]$

20. Which of the following complex is low spin?

- (1) All are low spin complexes
 (2) $[\text{Ni}(\text{CO})_4]$
 (3) $[\text{Pt}(\text{NH}_3)_4]^{2+}$
 (4) $[\text{Ni}(\text{NH}_3)_6]^{2+}$

Paragraph 7

If in the mixed carbonyl, the other ligand is also π acceptor, it would compete with the ligand CO for gaining the metal d_π electron charge. The higher is the extent of back donation in CO, the lesser will be the stretching vibration frequency for C—O bond. If PP_3 is better π -acceptor than CO, then answer the following.

21. Select the correct order of M—C bond order in the following molecule and ions:

- I. $[\text{Ni}(\text{CO})_4]$ II. $[\text{Co}(\text{CO})_4]^\ominus$
 III. $[\text{Fe}(\text{CO})_4]^{2-}$
 (1) $\text{I} > \text{II} > \text{III}$ (2) $\text{I} = \text{II} = \text{III}$
 (3) $\text{II} > \text{III} > \text{I}$ (4) $\text{I} < \text{II} < \text{III}$

22. Select the correct order of stretching vibration frequency C—O bond in following molecules:

- I. $[\text{Ni}(\text{CO})_4]$ II. $[\text{Ni}(\text{PF}_3)(\text{CO})_3]$
 (1) $\text{I} > \text{II}$ (2) $\text{I} < \text{II}$
 (3) $\text{I} = \text{II}$ (4) cannot be predicted

23. Select the correct order of C—O bond length in the following molecules:

- I. $[\text{Mo}(\text{CO})_3(\text{PF}_3)_3]$ II. $[\text{Mo}(\text{CO})_3(\text{PCl}_3)_3]$
 III. $[\text{Mo}(\text{CO})_3(\text{P}(\text{Me})_3)_3]$
 (1) $\text{I} > \text{II} > \text{III}$ (2) $\text{III} > \text{I} > \text{II}$
 (3) $\text{II} > \text{III} > \text{I}$ (4) $\text{I} < \text{II} < \text{III}$

Paragraph 8

Most of the metal carbonyls obey inert gas rule which states that the compounds in which the central metal atom appears to have attained the configuration of a noble gas either by the sharing or by the transfer of electrons tend to be more stable.

24. Which of the following has lowest C—O bond order?

- (1) $[\text{Mn}(\text{CO})_6]^\oplus$ (2) $[\text{Co}(\text{CO})_4]^\ominus$
 (3) $[\text{Fe}(\text{CO})_4]^2$ (4) $[\text{Ni}(\text{CO})_4]$

25. Select the correct order of C—O bond length of the following:

I. $[\text{M}(\text{CO})_3(\text{PF}_3)]$ II. $[\text{M}(\text{CO})_3(\text{PCl}_3)]$ III. $[\text{M}(\text{CO})_3(\text{PMe}_3)]$

- (1) $\text{I} < \text{II} < \text{III}$ (2) $\text{I} > \text{II} > \text{III}$
(3) $\text{I} = \text{II} = \text{III}$ (4) $\text{I} = \text{II} > \text{III}$

26. Which of the following has highest C—O bond length?

- (1) $[\text{Mn}(\text{CO})_6]^{\oplus}$ (2) $[\text{Co}(\text{CO})_4]^{\ominus}$
(3) $[\text{Fe}(\text{CO})_4]^2$ (4) $[\text{Ni}(\text{CO})_4]$

Paragraph 9

In the manufacture of iron, a gas (A) is formed in the zone of combustion of the blast furnace. The gas (A) reacted with coke in the zone of fusion to form another gas (B). X moles of (B) reacts with iron at 200°C and 100 atm pressure to form a compound (C).

27. The d orbital(s) involved in the formation of the complex (C) will be:

- (1) d_{z^2} (2) d_{xy} and $d_{x^2-y^2}$
(3) $d_{x^2-y^2}$ and d_{z^2} (4) $d_{x^2-y^2}$

28. The magnetic moment and effective atomic number of the C, respectively, are

- (1) 4.93 and 36 (2) 0 and 34
(3) 0 and 36 (4) None

Paragraph 10

The π acceptor ligands are those which possess vacant π -orbitals in addition to the lone pairs of electrons.

29. Which of the following complex ion has lowest M—C bond length?

- (1) $[\text{V}(\text{CO})_6]^{\ominus}$ (2) $[\text{Mn}(\text{CO})_6]^{\oplus}$
(3) $[\text{Ni}(\text{CO})_4]$ (4) $[\text{Fe}(\text{CO})_5]$

30. Which of the following complex ion has the highest C—O bond length?

- (1) $[\text{V}(\text{CO})_6]^{\ominus}$ (2) $[\text{Ni}(\text{CO})_4]$
(3) $[\text{Fe}(\text{CO})_5]$ (4) $[\text{Mn}(\text{CO})_6]^{\oplus}$

31. Which of the following complex/ion has lowest C—O bond order?

- (1) $[\text{V}(\text{CO})_6]^{\ominus}$ (2) $[\text{Ni}(\text{CO})_4]$
(3) $[\text{Fe}(\text{CO})_5]$ (4) $[\text{Mn}(\text{CO})_6]^{\oplus}$

32. Which of the following complex/ion has lowest M—C bond order?

- (1) $[\text{V}(\text{CO})_6]^{\ominus}$ (2) $[\text{Ni}(\text{CO})_4]$
(3) $[\text{Fe}(\text{CO})_5]$ (4) $[\text{Mn}(\text{CO})_6]^{\oplus}$

Paragraph 11

The π acid ligands donate their lone pairs to the metal to form a normal σ bond with the latter in addition to it, the vacant orbitals accept electrons from the filled metal orbitals to form a type of π -bond which supplements the σ bond.

33. Which of the following has lowest M—C bond length?

- (1) $[\text{Ni}(\text{CO})_4]$ (2) $[\text{Mn}(\text{CO})_6]^{\oplus}$
(3) $[\text{Fe}(\text{CO})_4]^2$ (4) $[\text{Co}(\text{CO})_4]^{\ominus}$

34. Which of the following has lowest M—C bond order?

- (1) $[\text{Fe}(\text{CO})_4]^2$ (2) $[\text{Co}(\text{CO})_4]^{\ominus}$
(3) $[\text{Ni}(\text{CO})_4]$ (4) $[\text{Mn}(\text{CO})_6]^{\oplus}$

35. Which of the following has lowest C—O bond length?

- (1) $[\text{Fe}(\text{CO})_4]^2$ (2) $[\text{Co}(\text{CO})_4]^{\ominus}$
(3) $[\text{Ni}(\text{CO})_4]$ (4) $[\text{Mn}(\text{CO})_6]^{\oplus}$

Paragraph 12

Coordination compound plays many important roles in animals and plants. They are essential in the storage and transport of oxygen, as electrons transfer agents, as catalysts, and in photosynthesis. Wide range of application in daily life takes place through formation of complexes. Photographic fixing, qualitative and quantitative analysis, purification of water, metallurgical extraction are some specific worth mentioning.

36. The complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ is formed in the brown ring test for nitrates when freshly prepared FeSO_4 solution is added to aqueous solution of NO_3^- followed by addition of conc. H_2SO_4 . Select correct statement about this complex:

- (1) Colour change is due to charge transfer
(2) It has iron in +1 oxidation state and nitrosyl as NO^{\oplus}
(3) It has magnetic moment of 3.87 BM confirming three unpaired electrons in Fe
(4) All the above are correct statements

37. Extraction of Ag from sulphide ore and removal of unreacted silver from photographic plate involve complexes:

- (1) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ in both
(2) $[\text{Ag}(\text{CN})_2]^{\ominus}$ in both
(3) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$, $[\text{Ag}(\text{CN})_2]^{\ominus}$
(4) $[\text{Ag}(\text{CN})_2]^{\ominus}$, $[\text{Ag}_2(\text{S}_2\text{O}_3)_2]^{3-}$

38. Lead poisoning in the body can be removed by

- (1) EDTA in the form of calcium dithyrogen salt
(2) Cis-platin (3) Zeisse's salt
(4) DMG

39. Cu^{2+} and Cd^{2+} both are precipitated as sulphides on passing H_2S gas in dil. HCl medium. However, precipitation of Cu^{2+} is prevented by

- (1) Adding excess of $\text{K}_4[\text{Fe}(\text{CN})_6]$ when Cd^{2+} is only precipitated
(2) Adding excess of KCN when Cu^{2+} forms stable complex $[\text{Cu}(\text{CN})_4]^{3-}$ and Cd^{2+} forms unstable complex $[\text{Cd}(\text{CN})_4]^{2-}$
(3) Adding KCNS when Cu^{2+} forms complex $[\text{Cu}(\text{CNS})_4]^2$ while Cd^{2+} does not form complex
(4) All of the above

40. Arrange the following in order of decreasing number of unpaired electrons:

- I. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ II. $[\text{Fe}(\text{CN})_6]^{3-}$
III. $[\text{Fe}(\text{CN})_6]^{4-}$ IV. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
(1) IV, I, II, III (2) I, II, III, IV
(3) III, II, I, IV (4) II, III, I, IV

Paragraph 13

Complex compound with empirical formula $\text{Co}_5\text{NH}_2\text{NO}_2\text{Br}_2$ exist in two isomers A (red) and B (yellow) 1 mole of each A and B gives 2 moles of AgBr when treated with excess of AgNO_3 .

1. A and B both can show.

- (1) Ionisation isomerism (2) Linkage isomerism
(3) Geometrical isomerism (4) Both (A) & (B)

2. Correct statement for A & B is:

- (1) Both A and B contain ONO^\ominus as ligand
(2) A contains NO_2^\ominus while B contains ONO^\ominus as ligand.
(3) A contains ONO^\ominus while B contains NO_2^\ominus as ligand.
(4) Both A and B contains NO_2^\ominus as ligands.

3. Correct statement for A & B is:

- (1) A and B both are paramagnetic
(2) A and B both are diamagnetic
(3) A is paramagnetic while B is diamagnetic
(4) A is diamagnetic while B is paramagnetic

Matrix Match Type

This section contains questions each with two columns I and II. Match the items given in column I with that in column II.

Column I	Column II
a. $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^\ominus$	p. Follow EAN
b. $[\text{Co}(\text{CO})_4]^\ominus$	q. Complex involved in synergic bonding
c. $[\text{V}(\text{CO})_6]^\ominus$	r. Complex having highest bond length of Co ligand
d. $[\text{Fe}(\text{CN})_5\text{C}(\text{CO})]^{3-}$	s. Complex having lowest bond length of Co ligand.

2. Match the complexes (in column I) with the type of isomerism (in column II).

Column I	Column II
a. $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]$	p. Optical
b. $\text{cis}[\text{Cr}(\text{en})_2\text{Cl}_2]$	q. Ionisation
c. $[\text{Cr}(\text{en})_2(\text{NO}_2)\text{Cl}]\text{SCN}$	r. Coordination
d. $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$	s. Geometrical

3.

Column I	Column II
a. $[\text{Cr}(\pi\text{-C}_6\text{H}_6)(\text{NO})_3]$	p. Coordination number of central metal is six.
b. $[\text{Cr}(\text{C}_2\text{H}_4)(\text{CO})_5]$	q. Bond order of all ligand decreases
c. $[\text{Pt}(\text{NO}_2)_2(\text{en})_2]^{2+}$	r. Stable according to EAN rule
d. $\text{Ir}(\text{SCN})(\text{SO}_4)(\text{NH}_3)_4$	s. Bond order of all M — L bond > 1.0
	t. Ligands acts as ambidentate

4. Match the column.

Column I	Column II
a. Two unpaired electron	p. $[\text{Ni}(\text{en})_3]^{2+}$
b. No unpaired electron	q. $[\text{VF}_6]^{3-}$
c. Optical isomerism	r. $[\text{NiCl}_2(\text{SCN})_4]^{4-}$
d. Inner orbital complex	s. $[\text{Fe}(\text{CN})_6]^{4-}$

5. Match the column.

Column I	Column II
a. $[\text{Cr}(\text{H}_2\text{O})_5\text{Br}]^{2+}$	p. Paramagnetic
b. $[\text{Cu}(\text{en})\text{Cl}_4]^{2-}$	q. Shows geometrical isomerism
c. $[\text{Pt}(\text{OX})_2]^{2-}$	r. Shows optical isomerism
d. $[\text{Fe}(\text{OH})_4]^\ominus$	s. Do not follow EAN rule
	t. Complex having symmetrical bidentate ligand

6. Match the column.

Column I	Column II (Number of unpaired electrons)
a. $[\text{Fe}(\text{NH}_3)_6]^{2+}$	p. 0
b. $[\text{MnO}_4]^\ominus$	q. 5
c. $[\text{Mn}(\text{NH}_3)_6]^{2+}$	r. 1
	s. 4

7. Match the column.

Column I (Complex ion)	Column II (Property which is different in given pair)
a. $\text{K}_4[\text{Ni}(\text{CN})_4]$ and $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$	p. Number of unpaired electrons
b. $\text{K}_4[\text{NiF}_6]$ and $\text{K}_2[\text{NiF}_6]$	q. Magnetic behaviour
c. $\text{K}_4[\text{Co}(\text{NO}_2)_6]$ and $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$	r. Hybridisation
	s. Geometry

8. Match the complex (in column I) with the geometry (in column II).

Column I (Complex ion)	Column II (Value charge on complex ion)
a. $[\text{Ni}(\text{dmg})_2]$	p. Tetrahedral
b. $[\text{ZnCl}_4]^{2-}$	q. Trigonal bipyramidal
c. $[\text{Co}(\text{NO}_2)_6]^{1-}$	r. Square planar
d. $[\text{Fe}(\text{CO})_5]$	s. Square pyramidal
	t. Octahedral

9. Match the column

Column I		Column II	
a.	Brown ring complex	p.	Octahedral
b.	Calcium nitroprusside	q.	$\mu_{MM} = 0 \text{ BM}$
c.	$\text{Ca}_2[\text{Fe}(\text{CN})_6]$	r.	$\mu_{MM} = \sqrt{15} \text{ BM}$
d.	Complex of Ag formed during its extraction	s.	NO^{\oplus} ligand

10. Match the column.

Column I (Type of complex)		Column II (The change in number of stereoisomer by the associated process with the given complex)	
a.	$[\text{Ma}_2\text{b}_2\text{c}_2]^{n\pm} \xrightarrow{-b/+d}$	p.	6
b.	$[\text{M}(\text{AB})_2\text{ab}]^{n\pm} \xrightarrow{-a/+b}$	q.	2
c.	$[\text{M}(\text{AA})_2\text{a}_2]^{n\pm} \xrightarrow{-a/+c}$	r.	5
d.	$[\text{M}(\text{AB})\text{a}_3\text{b}]^{n\pm} \xrightarrow{-a/+b}$	s.	3
		t.	0

11. Match the column.

Column I		Column II	
a.	$[\text{Ma}_3\text{bcd}]^{n\pm}$	p.	Four optically active isomer
b.	$[\text{M}(\text{AA})\text{b}_2\text{cd}]^{n\pm}$	q.	Four geometrical isomer
c.	$[\text{M}(\text{AB})_3]^{n\pm}$	r.	All geometrical isomers are optically active
d.	$[\text{M}(\text{AB})\text{b}_2\text{c}_2]^{n\pm}$	s.	Two pair of enantiomer
		t.	Two optically inactive isomer

Note: AA, BB, a, b, c, d are not having chiral centre.

12. Match the column.

Column I		Column II	
a.	$[\text{M}(\text{AA})\text{b}_2\text{cd}]$	p.	Complex molecule which shows optical isomerism
b.	$[\text{M}(\text{AAA})\text{b}_2\text{c}_2]$	q.	Only one cis and one trans isomer
c.	$[\text{M}(\text{AA})_2\text{b}_2]$	r.	Only one cis and two trans isomers
d.	$[\text{M}(\text{AA})_3]$	s.	Four geometrical isomers
		t.	Complex in which any cis isomer is optical active

13. Match the column.

Column I		Column II	
a.	$[\text{Ma}_4\text{bc}]$	p.	Six cis isomers
b.	$[\text{Ma}_2\text{b}_2\text{c}_2]$	q.	Four trans isomers

c.	$[\text{Ma}_2\text{bcde}]$	r.	Octahedral complex compound
d.	$[\text{Ma}_2\text{b}_2\text{cd}]$	s.	Four geometrical isomers
		t.	Only two geometrical isomer

14. Match the column.

Column I		Column II	
a.	$[\text{M}(\text{AB})_3]$	p.	Zero pair of enantiomers
b.	$[\text{M}(\text{AB})(\text{CD})\text{ef}]$	q.	Ten pair of enantiomers
c.	$[\text{Ma}_4\text{bc}]$	r.	Four number of stereoisomers
d.	$[\text{Ma}_3\text{b}_2\text{c}]$	s.	Four geometrical isomers

15. Match the column.

Column I		Column II	
a.	$[\text{Ma}_3\text{bcd}]$	p.	The number of stereoisomers is two
b.	$[\text{Ma}_3\text{b}_3]$	q.	The number of pair of enantiomer is zero
c.	$[\text{Mabcdef}]$	r.	The number of stereoisomers is five
d.	$[\text{Ma}_2\text{b}_2\text{c}_2]$	s.	The pair of enantiomer is one
		t.	The pair of enantiomer is fifteen

16. Match the column.

Column I		Column II	
a.	Hexachloridoplatinate(2-)	p.	Monodentate ligand is present in complex/ion
b.	Sodium diamminetetrahydroxyborate(III)	q.	Negative ligand is present in complex ion or molecule
c.	Tris(ethylenediamine)copper(II)	r.	Neutral ligand is present in complex ion/molecule sulphate
d.	Hexacarbonylmanganese hypobromate	s.	Central atom of complex or ion is a member of 3d transition series.
		t.	Octahedral structure of complex ion/molecule

17. Match the column.

Column I		Column II	
a.	$[\text{Fe}(\text{CN})_6]^{3-}$	p.	Optical isomerism
b.	$[\text{Cr}(\text{en})_2\text{Cl}_2]^{\oplus}$	q.	d^2sp^3 -hybridisation
c.	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	r.	d^2sp^3 hybridisation
d.	$[\text{CoF}_6]^{3-}$	s.	sp^3d^2 -hybridisation

18. Match the column.

Column I		Column II	
a.	$[\text{PtI}_2(\text{en})]$	p.	Square planar complex
b.	$[\text{Pt}(\text{NH}_3)_2\text{I}_2]$	q.	central atom is a member of 3d transition series
c.	$[\text{Pt}(\text{NH}_3)(\text{NO}_2)(\text{py})\text{NH}_2\text{OH}]$	r.	Complex which shows geometrical isomerism
d.	$[\text{Zn}(\text{gly})_2]$	s.	Non-planar complex
		t.	Both neutral as well as negative ligand are present in complex

19. Match the column.

Column I		Column II	
a.	$[\text{Cr}(\text{en})_2\text{I}_2]^{\oplus}$	p.	Complex molecule/ion in which neutral ligand is present
b.	$[\text{Pt}(\text{NH}_3)_2\text{I}_4]$	q.	Complex which shows geometrical isomerism
c.	$[\text{Cr}(\text{en})_3]^{3+}$	r.	d^2sp^3 -hybridisation is present in central atom of complex molecule/ion
d.	$[\text{Cr}(\text{gly})_3]$	s.	Two geometrical isomers
		t.	Complex in which only nitrogen atom acts as donor atom

20. Match the column.

Column I		Column II	
a.	$[\text{Co}(\text{NH}_3)_6]^{3+}$	p.	d^2sp^3 -hybridisation
b.	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	q.	Octahedral geometry

24. Match the items given in column I with that in Column II and III.

Column I		Column II		Column III	
Compound		No. of unpaired e^- s		Hybridisation shape & characteristics	
a.	$[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$	i.	Zero	p.	sp^3d^2 , octahedral
b.	$[\text{COF}_6]^{3-}$	ii.	3	q.	dsp^2 , square planar
c.	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	iii.	4	r.	sp^3 , tetrahedral
d.	$[\text{Ni}(\text{CO})_4]$	iv.	1	s.	Complex ion is formed in the brown ring test for NO_3^- ion

c.	$\text{K}_3[\text{Fe}(\text{CN})_6]$	r.	Blue colour due to charge transfer
d.	$\text{K}_4[\text{Fe}(\text{CN})_6]$	s.	Six electrons are present in t_{2g} orbitals
		t.	EAN is 36

21. Match the column.

Column I		Column II	
a.	$[\text{Cr}(\text{CN})_3(\text{NO}_2)_3]^{4-}$	p.	Outer orbital complex
b.	$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$	q.	Inner orbital complex
c.	$[\text{Fe}(\text{EDTA})]^-$	r.	$\mu = \sqrt{8}$ BM
d.	$[\text{Ni}(\text{en})_3]^{2+}$	s.	Shows optical activity


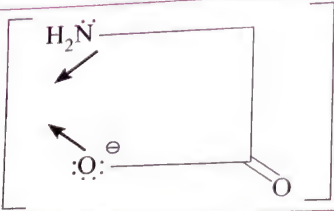
22. Match the column.

Column I		Column II	
a.	MnO_4^-	p.	sp^3 -hybridisation
b.	CrO_4^{2-}	q.	Tetrahedral structure
c.	$\text{Cr}_2\text{O}_7^{2-}$	r.	Diamagnetic but colourful species
d.	CrO_2Cl_2	s.	+6 oxidation state on central atom
		t.	all X-O bonds are identical (where X is central atom)

23. Match the column.

Column I		Column II	
a.	$[\text{Fe}(\text{CO})_4]^{2-}$	p.	Complex having lowest bond length of CO ligand
b.	$[\text{V}(\text{CO})_6]^-$	q.	Follow Sidgwick's rule of EAN
c.	$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$	r.	Synergic bonding is involved in complex/ion
d.	$[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$	s.	Complex having highest bond length of CO ligand
		t.	Organometallic compound

25. Match the items given in column I with that in Column II and III.

Column I		Column II		Column III	
Compound		No. of isomers		Type of isomerism	
a.	$[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})(\text{NO}_2)(\text{py})]^\oplus$	i.	1	p.	Optical
b.	$[\text{CoCl}_2(\text{NH}_3)_4]^\oplus + \text{Cl}^\ominus$ \downarrow $[\text{CoCl}_3(\text{NH}_3)_3] + \text{NH}_3$ (Number of isomers obtained for the complex product)	ii.	3	q.	Trans
c.	$[\text{Cr}(\text{edta})]^\ominus$	iii.	Zero	r.	Geometrical
d.		iv.	2	s.	None
e.	$[\text{Pt}(\text{gly})_2]$ where gly = glycinate 				

26. Match the items given in column I with that in Column II and III.

Column I		Column II		Column III	
Ions in complex species		Electronic configuration in crystal field theory		No. of unpaired e^- s	
a.	Fe^{+2} (In weak octahedral field ligand)	i.	t_{2g}^4, e_g^1	p.	4
b.	Fe^{+2} (In strong octahedral field ligand)	ii.	t_{2g}^4, e_g^2	q.	3
c.	Mn^{3+} (In weak octahedral field ligand)	iii.	t_{2g}^6, e_g^0	r.	Zero
d.	Mn^{3+} (In strong octahedral field ligand)	iv.	t_{2g}^3, e_g^1	s.	2
e.	Cr^{3+} (In weak and strong octahedral field ligand)	v.	t_{2g}^3, e_g^0		

27. Match the items given in column I with that in Column II and III.

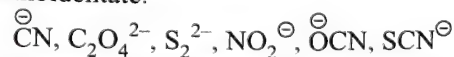
Column I		Column II		Column III	
Compound		Electronic configuration in crystal field theory		CFSE (Crystal field splitting energy)	
a.	$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (When $\Delta < p$)	i.	(e^2, t_2^3)	p.	$-0.6 \Delta_0$
b.	$[\text{FeCl}_4]^\ominus$ (When $\Delta < p$)	ii.	(e^2, t_2^0)	q.	$-1.6 \Delta_0 + P$
c.	$[\text{FeO}_4]^{2-}$ (When $\Delta < p$)	iii.	(t_{2g}^4, e_g^0)	r.	Zero
d.	$[\text{Cr}(\text{NH}_3)_6]^{2+}$ (When $\Delta > p$)	iv.	(t_{2g}^3, e_g^1)	s.	$-1.2 \Delta_t$

Numerical Value Type

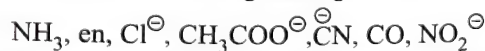
Naming and Terminology

- Give the number of ligand(s) in which donor atom is only N.
 $\text{NH}_2\text{CH}_2\text{COO}^\ominus$, en, dien, Py, EDTA, ph
- Give number of non-classical ligand which are negative ligands.
 CN^\ominus , $\text{S}_2\text{O}_3^{2-}$, $\text{C}_3\text{H}_5^\ominus$, $\text{C}_5\text{H}_5^\ominus$.
- Give the number of ligands which are negative as well as flexidentate.
 CO_3^{2-} , $\text{CH}_3\text{COO}^\ominus$, X^\ominus , H^\ominus , SO_4^{2-}

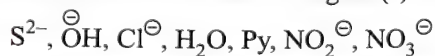
- Give the number of ligands which are monodentate as well as ambidentate.



- Give the number of strong field ligand(s) from the following:



- Give the number of weak field ligand(s) from the following:



- The sum of primary and secondary valencies of chromium in the complex $\text{CrBr}_3 \cdot 6\text{NH}_3$ is:

- Find the number of ligand(s) which is/are chelating.
en, $\text{C}_2\text{O}_4^{2-}$, acac, DMG, gly, ph

9. Find the number of ligand(s) which is/are polydentate ligand. en, dmg, dien, EDTA
10. How many coordinated water molecule(s) is/are present in brown ring complex?
11. Sodium nitroprusside is used to test S^{2-} ion. How many CN $^-$ ion acts as ligand in the compound.
12. Give the number of ligand(s) which is/are ambidentate and bidentate.
 S^{2-} , CN^- , OCN^- , $S_2O_3^{2-}$, $C_2O_4^{2-}$, S^{2-}
13. Give the number of ligand(s) which is/are non-classical ligand.
 CO , NO , C_2H_4 , $C_3H_5^+$, H^+
14. Give the number of ligand(s) which are monodentate, neutral as well as non-classical ligand.
 CO , CN^- , $S_2O_3^{2-}$, PF_3
15. Give the number of ligands which are non-classical ligand and π donor as well as π acceptor ligand.
 CO , PH_3 , PF_3 , $C_3H_5^+$, $C_5H_5^+$
16. What are the values of m and n in the anionic species $[V(CO)_m]^{n-}$, if it is following Sidwick EAN rule and having octahedral shape?
17. Consider the following carbonyl complex compounds
(I) $H_xCr(CO)_5$ (II) $CO_2(CO)_y$ (III) $Mo(CO)_z$
then calculate the value of $\left(\frac{x+y+z}{5}\right)$ is:
18. If x is total number of π bonds in ph (1,10-N, N-phenanthroline) and y is total number of lone pair e^- 's in ph and α -nitroso- β -naphthol. Then calculate the value of $\left(\frac{x+y}{4}\right)$.

Isomerism

19. Give the total number of possible isomers of $[ZnBr_2F_2]^{2-}$.
20. Give the number of pair of enantiomer of $[Ma_2b_2cd]$.
21. Give the total number of isomer of $[Be(gly)_2]$.
22. How many pairs of enantiomers are possible for $[M(AA)(BC)de]$?
23. Find the number of geometrical isomers in $[Co(en)(Pn)(NO_2)_2]$.

$$en = \begin{array}{c} CH_2-CH_2 \\ | \quad | \\ H_2N \quad NH_2 \end{array} \quad pn = \begin{array}{c} NH_2-CH_2-\overset{*}{CH}-NH_2 \\ | \\ CH_3 \end{array}$$
24. Write the sum of geometrical isomers in $[Pt(H_2N-CH(CH_3)-COO)_2]$ complex and stereoisomers of $[Pt(gly)_3]^+$ complex.
25. Write the sum of geometrical isomer in $[Ma_2b_2c_2]$ complex and stereoisomers in $[M(AB)_3]$ complex.

26. Give the ratio of geometrical isomers in $[M(AA)_2b_2]$ and optical isomers of $[M(AA)_3]$.
27. Give the number of geometrical isomer in $[Pt(gly)_2]$.
28. Give the total number of possible isomers of $[Co_2(CN)(NH_3)en]$.
29. Give the total number of possible isomers (*cis-trans* and optical) of $[CrCl_2 en_2]^+$.
30. Give the total number of possible structural isomers of the compound $[Cu(NH_3)_4][PtI_4]$.
31. Give the number of total possible coordination isomers in $[Pt(NH_3)_4][Cu(Br)_4]$.
32. Give the number of total possible ionisation isomers in $[Pt(NH_3)_4Cl_2]Br_2$.
33. Give the ratio of trans-isomers in $[M(AA)b_2c_2]$ (A) and $[Ma_4b_2]$ (B), respectively.

Hybridisation, VBT, CFT and Applications

34. In hexacyanidomanganate(II) ion the Mn atom assumes d^2sp^3 -hybrid states. Then the number of unpaired electrons in the complex is:
35. Give the number of unpaired electron(s) in the complex ion $[CoCl_6]^{3-}$.
36. Predict the number of unpaired electrons in a tetrahedral d^6 ion and in a square planar d^7 ion.
37. Give the number of unpaired electron present in the d-orbitals (whose lobes are present along the axis) for the complex $[Co(SCN)_4]^{2-}$.
38. Give the number of 3d electrons occupied in t_{2g} orbitals of hydrated Cr^{3+} ion (octahedral).
39. How many unpaired electrons are present in e_g orbital of MnO_4^- ?
40. How many electrons are present in d_{z^2} orbital of $[Ni(gly)_2]$?
41. Give the total number of t_{2g} and e_g electrons in $[NiF_6]^{2-}$.
42. How many electrons are present in d-orbitals which are present along the axis in $[Ti(H_2O)_6]^{3+}$?
43. If Hund's rule is violated, then how many unpaired electrons are present in $[Cr(NH_3)_6]^{3+}$ complex ion?
44. Give the number of unpaired electrons in t_{2g} set of d-orbitals in $[Co(H_2O)_3F_3]$ complex.
45. How many maximum atom(s) is/are present in same plane of $Cr(CO)_6$?
46. Find out the number of hydrogen bonds present in the structure of the nickel dimethylglyoxime complex.
47. How many e^- 's are present in t_{2g} set of d-orbitals of central metal cation in $[Fe(H_2O)_5NO]SO_4$ brown ring complex.

JEE MAIN

Single Correct Answer Type

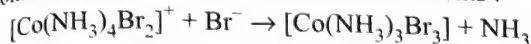
- Which of the following has an optical isomer?
 (1) $[\text{Co}(\text{NH}_3)_3\text{Cl}]^+$ (2) $[\text{Co}(\text{en})(\text{NH}_3)_2]^{2+}$
 (3) $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$ (4) $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$
 (AIEEE 2009)
- Which of the following pairs represents linkage isomers?
 (1) $[\text{Cu}(\text{NH}_3)_4] [\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4] [\text{CuCl}_4]$
 (2) $[\text{Pd}(\text{PPh}_3)_2 (\text{NCS})_2]$ and $[\text{Pd}(\text{PPh}_3)_2 (\text{SCN})_2]$
 (3) $[\text{Co}(\text{NH}_3)_5] \text{NO}_3\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$
 (4) $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}$ and $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$
 (AIEEE 2009)
- Which of the following has an optical isomer?
 (en = ethylenediamine)
 (1) $[\text{Zn}(\text{en})(\text{NH}_3)_2]^{2+}$ (2) $[\text{Co}(\text{en})_3]^{3+}$
 (3) $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$ (4) $[\text{Zn}(\text{en})_2]^{2+}$
 (AIEEE 2010)
- Which one of the following complex ions has geometrical isomers?
 (1) $[\text{Co}(\text{en})_3]^{3+}$ (2) $[\text{Ni}(\text{NH}_3)_5\text{Br}]^+$
 (3) $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$ (4) $[\text{Cr}(\text{NH}_3)_4(\text{en})]^{3+}$
 (AIEEE 2011)
- Which of the following facts about the complex $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is wrong?
 (1) The complex involves d^2sp^3 hybridization and is octahedral in shape.
 (2) The complex is paramagnetic.
 (3) The complex is an outer orbital complex.
 (4) The complex gives white precipitate with silver nitrate solution.
 (AIEEE 2011)
- The magnetic moment (spin only) of $[\text{NiCl}_4]^{2-}$ is:
 (1) 1.82 BM (2) 5.46 BM
 (3) 2.82 BM (4) 1.41 BM (AIEEE 2011)
- Among the ligands NH_3 , en, CN^- and CO, the correct order of their increasing field strength is
 (1) $\text{CO} < \text{NH}_3 < \text{en} < \text{CN}^-$ (2) $\text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$
 (3) $\text{CN}^- < \text{NH}_3 < \text{CO} < \text{en}$ (4) $\text{en} < \text{CN}^- < \text{NH}_3 < \text{CO}$
 (AIEEE 2011)
- Which among the following will be named as dibromidobis(ethylenediamine) chromium (III) bromide?
 (1) $[\text{Cr}(\text{en})_3]\text{Br}_3$ (2) $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$
 (3) $[\text{Cr}(\text{en})\text{Br}_4]^-$ (4) $[\text{Cr}(\text{en})\text{Br}_2]\text{Br}$
 (AIEEE 2012)
- Which of the following complex species is not expected to exhibit optical isomerism?
 (1) $[\text{Co}(\text{en})_3\text{Cl}_2]^+$ (2) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
 (3) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (4) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$
 (JEE Main 2013)
- The equation which is balanced and represents the correct product(s) is
 (1) $\text{Li}_2\text{O} + 2\text{KCl} \longrightarrow 2\text{LiCl} + \text{K}_2\text{O}$
 (2) $[\text{CoCl}(\text{NH}_3)_5]^+ + 5\text{H}^+ \longrightarrow \text{CO}^{2+} + 5\text{NH}_4^+ + \text{Cl}^-$
 (3) $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} + (\text{EDTA})^{4-} \xrightarrow{\text{excess NaOH}} [\text{Mg}(\text{EDTA})]^{2+} + 6\text{H}_2\text{O}$
 (4) $\text{CuSO}_4 + 4\text{KCN} \longrightarrow \text{K}_2[\text{Cu}(\text{CN})_4] + \text{K}_2\text{SO}_4$
 (JEE Main 2014)
- The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1 , L_2 , L_3 and L_4 absorbs wavelengths in the region of red, green, yellow, and blue, respectively. The increasing order of ligand strength of the four ligands is:
 (1) $L_4 < L_3 < L_2 < L_1$ (2) $L_1 < L_3 < L_2 < L_4$
 (3) $L_3 < L_2 < L_4 < L_1$ (4) $L_1 < L_2 < L_4 < L_3$
 (JEE Main 2014)
- The number of geometric isomers that can exist for square planar $[\text{Pt}(\text{Cl})(\text{py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+$ is (py = pyridine):
 (1) 2 (2) 3
 (3) 4 (4) 6
 (JEE Main 2015)
- Which of the following compounds is not colored yellow?
 (1) $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ (2) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$
 (3) $(\text{NH}_4)_3[\text{As}(\text{Mo}_3\text{O}_{10})_4]$ (4) BaCrO_4
 (JEE Main 2015)
- Which one of the following complexes shows optical isomerism?
 (1) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (2) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
 (3) *cis* $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ (4) *trans* $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$
 (en = ethylenediamine)
 (JEE Main 2016)
- The pair having the same magnetic moment is:
 [At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]
 (1) $[\text{CoCl}_4]^{2-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 (2) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$
 (3) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 (4) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
 (JEE Main 2016)
- On treatment of 100 mL of 0.1 M solution of $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$ with excess AgNO_3 , 1.2×10^{22} ions are precipitated. The complex is:
 (1) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (2) $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$
 (3) $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$ (4) $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
 (JEE Main 2017)

17. The oxidation states of Cr in $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{C}_6\text{H}_6)_2]$, and $\text{K}_2[\text{Cr}(\text{CN})_2(\text{O})_2(\text{O}_2)(\text{NH}_3)]$ respectively are :

- (1) +3, +2, and +4 (2) +3, 0, and +6
(3) +3, 0, and +4 (4) +3, +4, and +6

(JEE Main 2018)

18. Consider the following reaction and statements :



- (I) Two isomers are produced if the reactant complex ion is a *cis*-isomer.
(II) Two isomers are produced if the reactant complex ion is a *trans*-isomer.
(III) Only one isomer is produced if the reactant complex ion is a *trans*-isomer.
(IV) Only one isomer is produced if the reactant complex ion is a *cis*-isomer.

The correct statements are :

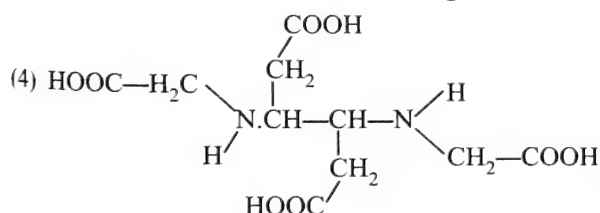
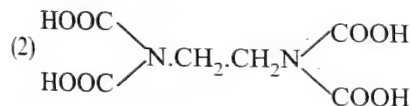
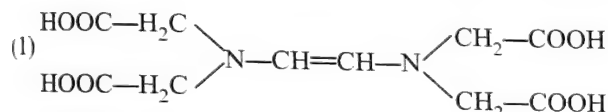
- (1) (I) and (III) (2) (III) and (IV)
(3) (II) and (IV) (4) (I) and (II)

(JEE Main 2018)

JEE ADVANCED

Single Correct Answer Type

1. The correct structure of ethylenediaminetetraacetic acid (EDTA) is



(IIT-JEE 2010)

2. The ionisation isomer of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$ is

- (1) $[\text{Cr}(\text{H}_2\text{O})_4(\text{O}_2\text{N})]\text{Cl}_2$
(2) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$
(3) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$
(4) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)]\text{H}_2\text{O}$

(IIT-JEE 2010)

3. The complex showing a spin-magnetic moment of 2.82 BM is

- (1) $\text{Ni}(\text{CO})_4$ (2) $[\text{NiCl}_4]^{2-}$
(3) $\text{Ni}(\text{PPh}_3)_4$ (4) $[\text{Ni}(\text{CN})_4]^{2-}$

(IIT-JEE 2010)

4. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^- , CN^- and H_2O , respectively, are

- (1) Octahedral, tetrahedral and square planar
(2) Tetrahedral, square planar and octahedral
(3) Square planar, tetrahedral and octahedral
(4) Octahedral, square planar and octahedral

(IIT-JEE 2011)

5. Among the following complexes (K–P)

$\text{K}_3[\text{Fe}(\text{CN})_6]$ (K), $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (L),
 $\text{Na}_3[\text{Co}(\text{oxalate})_3]$ (M), $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ (N),
 $[\text{Pt}(\text{CN})_4]$ (O) and $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (P)

The diamagnetic complexes are

- (1) K, L, M, N (2) K, M, O, P
(3) L, M, O, P (4) L, M, N, O

(IIT-JEE 2011)

6. As per IUPAC nomenclature, the name of the complex $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$ is

- (1) Tetraaquadiammincobalt(III) chloride
(2) Tetraaquadiammincobalt(III) chloride
(3) Diaminetetraaquacobalt(III) chloride
(4) Diamminetetraaquacobalt(III) chloride

(IIT-JEE 2012)

7. The colour of light absorbed by an aqueous solution of CuSO_4 is

- (1) orange-red (2) blue-green
(3) yellow (4) violet

(IIT-JEE 2012)

8. $[\text{NiCl}_2\{\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\}_2]$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively

- (1) Tetrahedral and tetrahedral
(2) Square planar and square planar
(3) Tetrahedral and square planar
(4) Square planar and tetrahedral

(IIT-JEE 2012)

9. Which of the following complexes is **not** expected to exhibit optical isomerism?

- (1) $[\text{Co}(\text{en})_2\text{Cl}_2]^{\oplus}$ (2) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
(3) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^{\oplus}$ (4) $[\text{Co}(\text{en})_3]^{3+}$

(JEE Advanced 2013)

10. Consider the following complexes ions, P, Q and R

$\text{P} = [\text{FeF}_6]^{3-}$, $\text{Q} = [\text{V}(\text{H}_2\text{O})_6]^{2+}$ and $\text{R} = [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

The correct order of the complex ions, according to their spin only magnetic moment values (in BM) is

- (1) $\text{R} < \text{Q} < \text{P}$ (2) $\text{Q} < \text{R} < \text{P}$
(3) $\text{R} < \text{P} < \text{Q}$ (4) $\text{Q} < \text{P} < \text{R}$

(JEE Advanced 2013)

11. An excess of AgNO_3 is added to 100 mL of a 0.01 M solution of dichlorotetraaquachromium(III) chloride. The number of moles of AgCl precipitated would be

- (1) 0.003 (2) 0.01
(3) 0.001 (4) 0.002

(JEE Advanced 2013)

12. The equation which is balanced and represents the correct product(s) is

- (1) $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} + (\text{EDTA})^{4-} \xrightarrow{\text{Excess NaOH}} [\text{Mg}(\text{EDTA})]^{2-} + 6\text{H}_2\text{O}$
 (2) $\text{CuSO}_4 + 4\text{KCN} \longrightarrow \text{K}_2[\text{Cu}(\text{CN})_4] + \text{K}_2\text{SO}_4$
 (3) $\text{Li}_2\text{O} + 2\text{KCl} \longrightarrow 2\text{LiCl} + \text{K}_2\text{O}$
 (4) $[\text{CoCl}(\text{NH}_3)_5]^\oplus + 5\text{H}^\oplus \longrightarrow \text{Co}^{2+} + 5\text{NH}_4^\oplus + \text{Cl}^\ominus$

(JEE Advanced 2014)

13. The number of geometric isomers that can exist for square planar $[\text{Pt}(\text{Cl})(\text{py})(\text{NH}_3)(\text{NH}_2\text{OH})]^\oplus$ is (py = pyridine):

- (1) 2 (2) 3
(3) 4 (4) 6

(JEE Advanced 2015)

14. Among $[\text{Ni}(\text{CO})_4]$, $[\text{NiCl}_4]^{2-}$, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, $\text{Na}_3[\text{CoF}_6]$, Na_2O_2 and CsO_2 , the total number of paramagnetic compounds is

- (1) 2 (2) 3
(3) 4 (4) 5 (JEE Advanced 2016)

15. The geometries of the ammonia complexes of Ni^{2+} , Pt^{2+} and Zn^{2+} , respectively, are

- (1) octahedral, square planar and tetrahedral
 (2) square planar, octahedral and tetrahedral
 (3) tetrahedral, square planar and octahedral
 (4) octahedral, tetrahedral and square planar

(JEE Advanced 2016)

Multiple Correct Answers Type

1. The pair of coordination complexes/ions exhibiting the same kind of isomerism is (are)

- (1) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
 (2) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^\oplus$ and $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^\oplus$
 (3) $[\text{CoBr}_2\text{Cl}_2]^{2-}$ and $[\text{PtBr}_2\text{Cl}_2]^{2-}$
 (4) $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$

(JEE Advanced 2013)

2. Addition of excess aqueous ammonia to a pink coloured aqueous solution of $\text{MCl}_2 \cdot 6\text{H}_2\text{O}(\text{X})$ and NH_4Cl gives an octahedral complex **Y** in the presence of air. In aqueous solution, complex **Y** behaves as 1 : 3 electrolyte. The reaction of **X** with excess HCl at room temperature results in the formation of a blue coloured complex **Z**. The calculated spin only magnetic moment of **X** and **Z** is 3.87 B.M., whereas it is zero for complex **Y**.

Among the following options, which statement(s) is(are) correct?

- (1) The hybridization of the central metal ion in **Y** is d^2sp^3 .
 (2) **Z** is a tetrahedral complex
 (3) Addition of silver nitrate to **Y** gives only two equivalents of silver chloride.

(4) When **X** and **Z** are in equilibrium at 0°C , the colour of the solution is pink

(JEE Advanced 2017)

3. The correct option(s) regarding the complex $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ (en = $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) is (are)

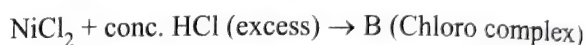
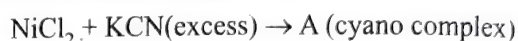
- (1) It has two geometrical isomers
 (2) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands
 (3) It is paramagnetic
 (4) It absorbs light at longer wavelength as compared to $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$

(JEE Advanced 2018)

Linked Comprehension Type

Paragraph 1

The coordination number of Ni^{2+} is 4.



1. The IUPAC name of A and B are

- (1) potassium tetracyanonickelate (II), potassium tetrachloronickelate (II).
 (2) tetracyanopotassiumnickelate (II), tetrachloropotassiumnickelate (II).
 (3) tetracyanonickel(II) tetrachloronickel(II)
 (4) potassium tetracyanonickel(II), tetrachloronickel (II).

2. Predict the magnetic nature of A and B:

- (1) Both are diamagnetic.
 (2) A is diamagnetic and B is paramagnetic with one unpaired electron.
 (3) A is diamagnetic and B is paramagnetic with two unpaired electrons.
 (4) Both are paramagnetic.

3. The hybridisation of A and B are

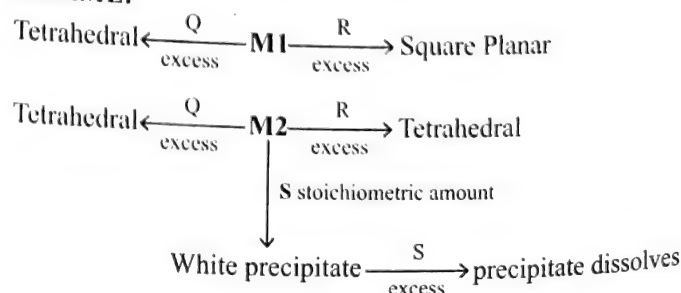
- (1) dsp^2 , sp^3 (2) sp^3 , sp^3
 (3) dsp^2 , dsp^2 (4) sp^3d^2 , d^2sp^3

(IIT-JEE 2006)

Paragraph 2

An aqueous solution of metal ion **M1** reacts separately with reagents **Q** and **R** in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion **M2** always forms tetrahedral complexes with these reagents. Aqueous solution of **M2** on reaction with reagent **S** gives white precipitate which dissolves in excess of **S**. The reactions are summarised in the scheme given below:

SCHEME:



4. M1, Q and R, respectively are

- (1) Zn^{2+} , KCN and HCl (2) Ni^{2+} , HCl and KCN
(3) Cd^{2+} , KCN and HCl (4) Co^{2+} , HCl and KCN

5. Reagent S is

- (1) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (2) Na_2HPO_4
(3) K_2CrO_4 (4) KOH

(JEE Advanced 2014)

Matrix Match Type

1. Match the complexes in **Column I** with their properties listed in **Column II**.

Column I	Column II
a. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$	p. Geometrical isomers
b. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	q. Paramagnetic
c. $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}$	r. Diamagnetic
d. $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$	s. Metal ion with +2 oxidation state

(IIT-JEE 2007)

2. Match each coordination compound in **Column I** with an appropriate pair of characteristics from **Column II** and select the correct answer using the code given below the lists.

Column I	Column II
a. $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	p. Paramagnetic and exhibits ionisation isomerism
b. $[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}](\text{NO}_3)_2$	q. Diamagnetic and exhibits cis-trans isomerism
c. $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]\text{NO}_3$	r. Paramagnetic and exhibits cis-trans isomerism
d. $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{NO}_3$	s. Diamagnetic and exhibits ionisation isomerism

Code:

- | | | | | |
|-----|---|---|---|---|
| | a | b | c | d |
| (1) | s | q | r | p |
| (2) | r | p | s | q |
| (3) | q | p | r | s |
| (4) | p | r | s | q |

(JEE Advanced 2014)

3. Match the catalysts to the correct processes:

Catalyst	Process
a. TiCl_3	i. Wacker process
b. PdCl_2	ii. Ziegler-Natta polymerization
c. CuCl_2	iii. Contact process
d. V_2O_5	iv. Deacon's process

(1) a. - iii., b. - ii., c. - iv., d. - i.

(2) a. - ii., b. - i., c. - iv., d. - iii.

(3) a. - ii., b. - iii., c. - iv., d. - i.

(4) a. - iii., b. - i., c. - ii., d. - iv.

(JEE Advanced 2015)

4. Match each set of hybrid orbitals from List-I with complex(es) given List-II.

List-I	List-II
P. dsp^2	1. $[\text{FeF}_6]^{4+}$
Q. sp^3	2. $[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$
R. sp^3d^2	3. $[\text{Cr}(\text{NH}_3)_6]^{3+}$
S. d^2sp^3	4. $[\text{FeCl}_4]^{2-}$
	5. $\text{Ni}(\text{CO})_4$
	6. $[\text{Ni}(\text{CN})_4]^{2-}$

The correct option is

(1) $\text{P} \rightarrow 5$; $\text{Q} \rightarrow 4, 6$; $\text{R} \rightarrow 2, 3$; $\text{S} \rightarrow 1$

(2) $\text{P} \rightarrow 5, 6$; $\text{Q} \rightarrow 4$; $\text{R} \rightarrow 3$; $\text{S} \rightarrow 1, 2$

(3) $\text{P} \rightarrow 6$; $\text{Q} \rightarrow 4, 5$; $\text{R} \rightarrow 1$; $\text{S} \rightarrow 2, 3$

(3) $\text{P} \rightarrow 4, 6$; $\text{Q} \rightarrow 5, 6$; $\text{R} \rightarrow 1, 2$; $\text{S} \rightarrow 3$

(JEE Advanced 2018)

Numerical Value Type

1. The volume (in mL) of 0.1M AgNO_3 required for complete precipitation of Cl^- ions present in 30 mL of 0.01M solution of $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$, as silver chloride is close to

(IIT-JEE 2011)

2. EDTA^{4-} is ethylenediamine tetraacetate ion. The total number of N-Co-O bond angles in $[\text{Co}(\text{EDTA})]^{-1}$ complex ion is

(JEE Advanced 2013)

3. In the complex acetyl bromodidodicarbonylbis(triethylphosphine) iron(II), the number of Fe-C bond(s) is

(JEE Advanced 2015)

4. Among the complex ions, $[\text{Co}(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2)_2\text{Cl}_2]^+$, $[\text{CrCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$, $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$, $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$, $[\text{Co}(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2)_2(\text{NH}_3)\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$, the number of complex ion(s) that show(s) cis-trans isomerism is

(JEE Advanced 2015)

5. In dilute aqueous H_2SO_4 , the complex diaquodioxalatoferate(II) is oxidized by MnO_4^- . For this reaction, the ratio of the rate of change of $[\text{H}^+]$ to the rate of change of $[\text{MnO}_4^-]$ is

(JEE Advanced 2015)

6. For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the

difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is [Atomic number of Fe = 26] (JEE Advanced 2015)

7. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a

strong electrolyte) is -0.0558°C , the number of chloride(s) in the coordination sphere of the complex is
[K_f of water = $1.86 \text{ K kg mol}^{-1}$] (JEE Advanced 2015)

8. The number of geometric isomers possible for the complex $[\text{CoL}_2\text{Cl}_2]$ ($\text{L} = \text{H}_2\text{NCH}_2\text{CH}_2\text{O}^-$) is (JEE Advanced 2016)

Answers Key

EXERCISES

Single Correct Answer Type

- | | | | | |
|----------|----------|----------|----------|----------|
| 1. (2) | 2. (4) | 3. (1) | 4. (4) | 5. (3) |
| 6. (2) | 7. (1) | 8. (4) | 9. (1) | 10. (2) |
| 11. (2) | 12. (1) | 13. (3) | 14. (3) | 15. (4) |
| 16. (1) | 17. (2) | 18. (1) | 19. (3) | 20. (1) |
| 21. (1) | 22. (2) | 23. (1) | 24. (3) | 25. (2) |
| 26. (3) | 27. (2) | 28. (1) | 29. (3) | 30. (3) |
| 31. (3) | 32. (3) | 33. (4) | 34. (3) | 35. (4) |
| 36. (2) | 37. (1) | 38. (1) | 39. (1) | 40. (4) |
| 41. (2) | 42. (2) | 43. (4) | 44. (2) | 45. (4) |
| 46. (2) | 47. (2) | 48. (3) | 49. (1) | 50. (3) |
| 51. (1) | 52. (2) | 53. (3) | 54. (3) | 55. (3) |
| 56. (3) | 57. (3) | 58. (2) | 59. (1) | 60. (2) |
| 61. (3) | 62. (2) | 63. (1) | 64. (2) | 65. (3) |
| 66. (2) | 67. (2) | 68. (2) | 69. (2) | 70. (1) |
| 71. (3) | 72. (3) | 73. (3) | 74. (2) | 75. (4) |
| 76. (2) | 77. (2) | 78. (2) | 79. (3) | 80. (3) |
| 81. (4) | 82. (4) | 83. (4) | 84. (4) | 85. (1) |
| 86. (1) | 87. (2) | 88. (4) | 89. (1) | 90. (4) |
| 91. (3) | 92. (2) | 93. (2) | 94. (2) | 95. (3) |
| 96. (4) | 97. (3) | 98. (4) | 99. (2) | 100. (4) |
| 101. (2) | 102. (1) | 103. (3) | 104. (1) | 105. (2) |
| 106. (1) | 107. (2) | 108. (3) | 109. (2) | 110. (4) |
| 111. (4) | 112. (2) | 113. (3) | 114. (2) | 115. (4) |
| 116. (2) | 117. (1) | 118. (3) | 119. (1) | 120. (1) |
| 121. (1) | 122. (1) | 123. (3) | 124. (2) | 125. (1) |
| 126. (3) | 127. (2) | 128. (1) | 129. (4) | 130. (2) |
| 131. (1) | 132. (1) | 133. (3) | 134. (1) | 135. (1) |
| 136. (4) | 137. (3) | 138. (1) | 139. (3) | 140. (1) |
| 141. (4) | 142. (3) | 143. (3) | 144. (1) | 145. (2) |
| 146. (2) | 147. (3) | 148. (1) | 149. (4) | 150. (2) |
| 151. (2) | 152. (1) | 153. (2) | 154. (3) | 155. (3) |
| 156. (2) | 157. (2) | 158. (2) | 159. (3) | 160. (1) |
| 161. (1) | 162. (4) | 163. (1) | 164. (1) | 165. (4) |
| 166. (2) | 167. (1) | 168. (2) | 169. (1) | 170. (3) |
| 171. (1) | 172. (3) | 173. (1) | 174. (4) | 175. (1) |
| 176. (1) | 177. (2) | 178. (3) | 179. (1) | 180. (1) |
| 181. (3) | 182. (3) | 183. (1) | | |

Multiple Correct Answers Type

- | | | |
|------------------|---------------|------------------|
| 1. (1, 2) | 2. (1, 2, 3) | 3. (1, 2) |
| 4. (1, 2, 3, 4) | 5. (1, 2, 3) | 6. (1, 2, 3) |
| 7. (1, 2, 3, 4) | 8. (1, 2, 3) | 9. (1, 2, 3) |
| 10. (1, 2, 3, 4) | 11. (1, 2, 3) | 12. (1, 3, 4) |
| 13. (1, 2, 3) | 14. (2, 3, 4) | 15. (1, 4) |
| 16. (2, 3, 4) | 17. (2, 3, 4) | 18. (1, 2, 3) |
| 19. (1, 2, 3) | 20. (2, 3) | 21. (2, 3) |
| 22. (1) | 23. (2, 3) | 24. (1, 2, 3, 4) |
| 25. (1, 4) | 26. (1, 2, 4) | 27. (1, 2, 3, 4) |
| 28. (2, 3, 4) | 29. (1, 2, 4) | 30. (2, 4) |
| 31. (2, 3, 4) | 32. (2, 3) | 33. (1, 2, 4) |
| 34. (3, 4) | 35. (1, 2, 3) | 36. (2, 3, 4) |
| 37. (1, 3, 4) | 38. (1, 2) | 39. (1, 2) |
| 40. (2, 3, 4) | 41. (2, 3) | 42. (1, 2, 3, 4) |
| 43. (1, 2, 3, 4) | 44. (1, 2, 3) | 45. (1, 2, 4) |
| 46. (1, 2) | 47. (1, 2, 3) | 48. (1, 2, 4) |
| 49. (1, 2) | 50. (1, 2, 3) | 51. (2, 3, 4) |
| 52. (2, 3, 4) | 53. (1, 2, 3) | 54. (1, 2) |

Linked Comprehension Type

- | | | | | |
|---------|------------|---------------|------------|---------|
| 1. (1) | 2. (2) | 3. (2) | 4. (3) | 5. (2) |
| 6. (2) | 7. (3) | 8. (1) | 9. (2) | 10. (1) |
| 11. (3) | 12. (1, 4) | 13. (2, 3, 4) | 14. (3, 4) | 15. (2) |
| 16. (2) | 17. (2) | 18. (4) | 19. (1) | 20. (3) |
| 21. (4) | 22. (2) | 23. (4) | 24. (3) | 25. (1) |
| 26. (3) | 27. (1) | 28. (3) | 29. (1) | 30. (1) |
| 31. (1) | 32. (1) | 33. (3) | 34. (4) | 35. (4) |
| 36. (4) | 37. (4) | 38. (1) | 39. (2) | 40. (1) |
| 41. (4) | 42. (3) | 43. (3) | | |

Matrix Match Type

Q.No.	a	b	c	d	e	f
1.	q	p, q, r	q	p, q, s	—	—
2.	s	p	q	r	—	—
3.	q, r, s	p, q, r, s	p, r	p, r, t	—	—
4.	p, q, r	s,	p	q, s	—	—
5.	p, s	p, s, t	s, t	p, s	—	—
6.	s	p	q	—	—	—

7.	r, s	p	p	—	—	—
8.	r	p	t	q	—	—
9.	p, r, s	p, q, s	p, q	q	—	—
10.	p	r	t	p	—	—
11.	q	p, q, s, t	p, r, s	p, q, s, t	—	—
12.	p, s, t	p, r, t	p, q, t	p	—	—
13.	r, t	q, r	p, r, s	q, r	—	—
14.	r, s	q	s	p	—	—
15.	r, s	p, q	t	s	—	—
16.	p, q, t	p, q, r, s, t	r, s, t	p, r, s, t	—	—
17.	q, r	p, q, r	r, s	r, s	—	—
18.	p, t	p, r, t	p, r, t	q, s	—	—
19.	p, q, r, s	p, q, r, s	p, r, t	q, r, s	—	—
20.	p, q, s, t	p, q, r, s, t	p, q	p, q, s, t	—	—
21.	q, r	q, s	q, s	p, r, s	—	—
22.	p, q, r, t	p, q, r, s, t	p, q, r, s	p, q, r, s, t	—	—
23.	q, r, s, t	p, q, r, t	r, t	r	—	—
24.	ii-p, s	iii-p	iv-q	i-r		
25.	ii-r	i-q	iv-p	iii-s	iv-r	
26.	ii-p	iii-r	iv-p	i-s	v-q	
27.	iv-p	i-r	ii-s	iii-q		

Numerical Value Type

- | | | | | |
|------------|------------|------------|---------|---------|
| 1. (4) | 2. (3) | 3. (3) | 4. (4) | 5. (5) |
| 6. (5) | 7. (9) | 8. (6) | 9. (2) | 10. (5) |
| 11. (5) | 12. (1) | 14. (4) | 14. (2) | 15. (2) |
| 16. (6, 1) | 17. (2, 4) | 18. (3, 5) | 19. (2) | 20. (2) |
| 21. (2) | 22. (5) | 23. (5) | 24. (8) | 25. (9) |
| 26. (1) | 27. (2) | 28. (8) | 29. (3) | 30. (4) |
| 31. (4) | 32. (3) | 33. (2) | 34. (1) | 35. (4) |

- | | | | | |
|------------|---------|---------|---------|---------|
| 36. (4, 1) | 37. (0) | 38. (3) | 39. (0) | 40. (2) |
| 41. (6) | 42. (0) | 43. (1) | 44. (2) | 45. (9) |
| 46. (2) | 47. (5) | | | |

ARCHIVES

JEE Main

Single Correct Answer Type

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (4) | 2. (2) | 3. (2) | 4. (3) | 5. (3) |
| 6. (3) | 7. (2) | 8. (2) | 9. (3) | 10. (2) |
| 11. (2) | 12. (2) | 13. (1) | 14. (3) | 15. (3) |
| 16. (4) | 17. (2) | 18. (1) | | |

JEE Advanced

Single Correct Answer Type

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (3) | 2. (2) | 3. (4) | 4. (2) | 5. (3) |
| 6. (4) | 7. (1) | 8. (3) | 9. (2) | 10. (2) |
| 11. (3) | 12. (4) | 13. (2) | 14. (2) | 15. (1) |

Multiple Correct Answers Type

- | | | |
|-----------|--------------|--------------|
| 1. (2, 4) | 2. (1, 2, 4) | 3. (1, 2, 3) |
|-----------|--------------|--------------|

Linked Comprehension Type

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (1) | 2. (3) | 3. (1) | 4. (2) | 5. (4) |
|--------|--------|--------|--------|--------|

Matrix Match Type

- (a \rightarrow p, q, s; b \rightarrow p, r, s; c \rightarrow q, s; d \rightarrow q, s)
- (2)
- (2)
- (3)

Numerical Value Type

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (3) | 2. (6) | 3. (3) | 4. (6) | 5. (8) |
| 6. (4) | 7. (1) | 8. (5) | | |

8

Qualitative Inorganic Salt Analysis

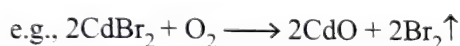
OVERVIEW

1. Analysis of a substance to identify its constituent ions (anions and cations) is known as **qualitative analysis**.
2. Determination of the amounts of its component in a given sample is known as **quantitative analysis**.
3. **Effect of heating of salt (when a gas is evolved)**

a. Coloured gas:

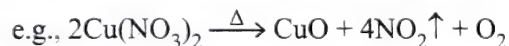
- i. Br₂ (Reddish brown) turns starch paper yellow.

Substance: Bromide



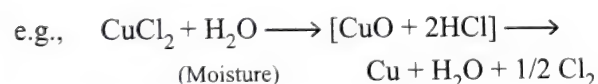
- ii. NO₂ (Brown) turns starch iodine paper blue.

Substance: Nitrites and nitrates of heavy metals



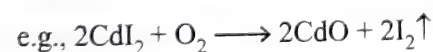
- iii. Cl₂ (Greenish yellow) bleaches moist litmus paper.

Substance: Chlorides



- iv. I₂ (Violet) turns starch paper blue.

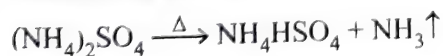
Substance: Iodide



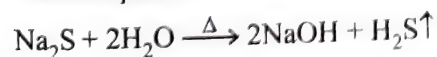
b. Colourless with odour gas:

- i. NH₃ – Turns red litmus blue.

Ammonium salts

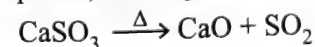


- ii. H₂S – Smell of rotten egg, turns lead acetate paper black sulphides.



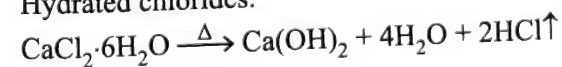
- iii. SO₂ – Smell of burning sulphur, turns acidified K₂Cr₂O₇ paper green.

Sulphites, thiosulphates



- iv. HCl – Pungent smell, white fumes with ammonia

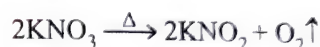
Hydrated chlorides.



c. Colourless and odourless gas:

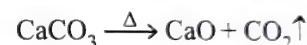
- i. O₂ – Supports glowing.

Alkali nitrates



- ii. CO₂ – Turns lime water milky.

Carbonates / Oxalates



4. Colour change on heating and cooling.

(Refer to Section 8.3.1.)

5. Substance sublimes and colour of sublimate:

Yellow	As ₂ S ₃ , HgI ₂ turns red on rubbing with glass rod
White	HgCl ₂ , Hg ₂ Cl ₂ , AlCl ₃ , As ₂ O ₃ , Sb ₂ O ₃
Blue black or violet	Iodides

6. Substance swells on heating:

Alums, borates, borax and phosphates

7. Substance makes crackling noise on heating:

NaCl, KI, Pb(NO₃)₂, Ba(NO₃)₂

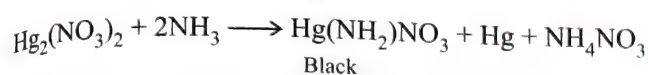
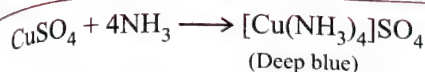
8. Substance melts on heating:

Salts of alkali metals and salts having water of crystallisation.

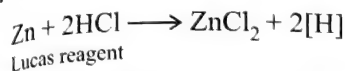
9. Acid radicals:

a. Radicals tested by dilute HCl/H₂SO₄:

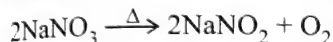
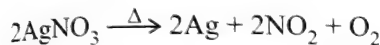
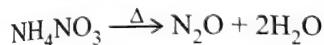
Acid radicals	Gas evolved
CO ₃ ²⁻	CO ₂
SO ₃ ²⁻	SO ₂
S ²⁻	H ₂ S
NO ₂ ⁻	NO ₂ + NO
CH ₃ COO ⁻	CH ₃ COOH vapours



vii. All nitrates and nitrites on reduction will give ammonia



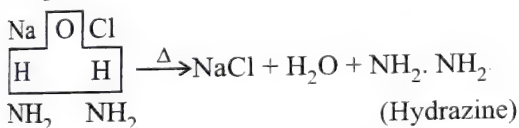
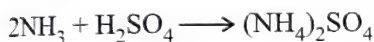
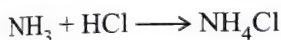
viii. All nitrates on decomposition give oxygen, metal oxide, NO_2 except:



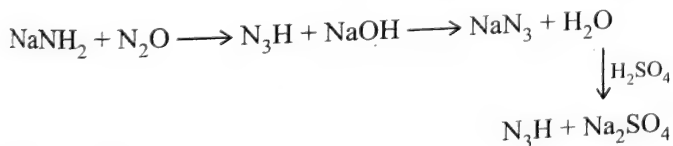
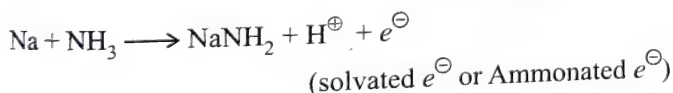
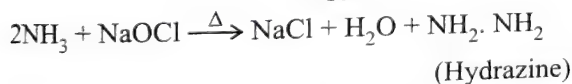
ix. All nitrites on decomposition give nitrogen, except



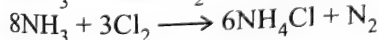
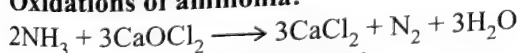
x. Some properties of NH_3 :



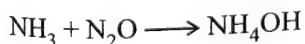
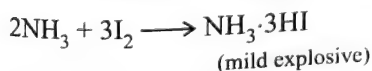
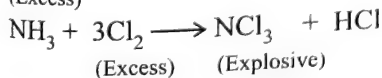
OR



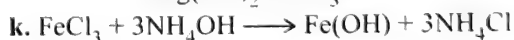
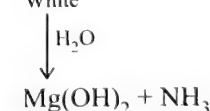
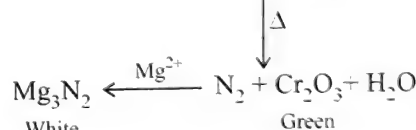
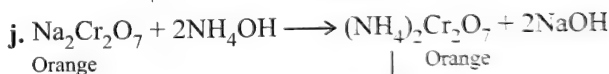
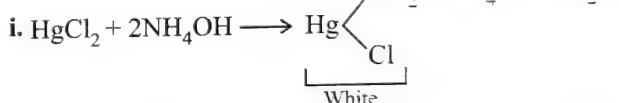
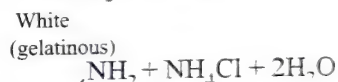
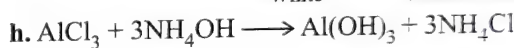
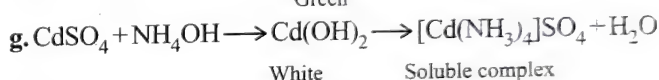
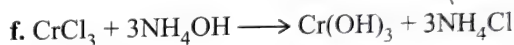
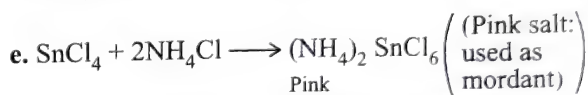
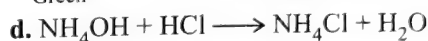
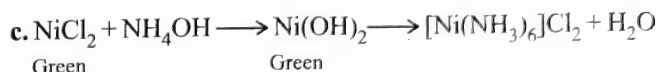
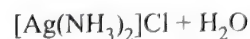
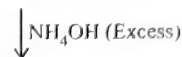
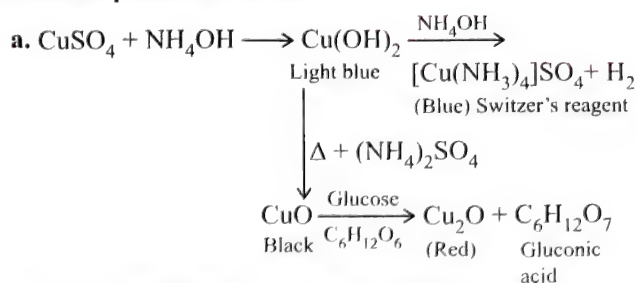
xi. Oxidations of ammonia:



(Excess)

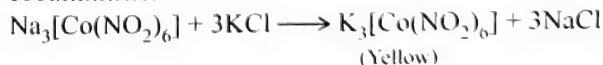


xii. Some important reactions:

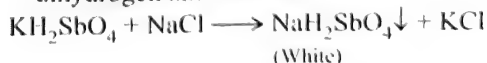


Red/Brown

l. Potassium salts give yellow precipitate with sodium cobaltinitrite.



m. Sodium salts give thick white precipitate with potassium dihydrogen antimonate.



8.1 INTRODUCTION

Qualitative inorganic analysis is an important part of chemistry. The purpose of this topic is to identify the constituent ions — **anions** (also called **acid radicals**) and cations (also called **basic radicals**). The analysis may be performed by physical, physico-chemical and chemical methods. In chemical method of analysis, the constituent ion is usually converted into another compound of known characteristics and the parent ion is thereby inferred.

8.2 SYSTEMATIC QUALITATIVE ANALYSIS

Every analysis is divided into three parts:

- 1. The preliminary examination:** This includes preliminary examinations such as colour, effect of heating, flame test, borax bead test, charcoal cavity test, cobalt nitrate test, and heating with dilute and concentrated sulphuric acid.
- 2. The examination of anions in solution.**
- 3. The examination of cations in solution.**

Preliminary examinations are generally useful in the case of simple salt. When a mixture of salts is present in a given sample, the tests generally interfere and give mixed up response. However, heating with dilute and conc. H_2SO_4 gives indications for the presence of some anions which are confirmed by wet test.

The analysis of basic radicals (cations) is systematic, whereas that of acidic radicals is slightly haphazard.

Acid radicals are analysed first followed by basic radicals, as presence of some acid radicals (known as interfering radicals) creates unwanted problems and therefore their removal become essential at appropriate places.

8.2.1 ANALYSIS OF ACID RADICALS (ANIONS)

Systematic identification of anions involves the following steps:

- 1. Preliminary tests with dilute $\text{H}_2\text{SO}_4/\text{HCl}$.**
- 2. Preliminary tests with conc. H_2SO_4 .**
- 3. Confirmatory test:** Having made a preliminary guess about the presence of anions, confirmation is done by specific tests.
- 4. Tests based on reactions in solution:** Some anions like SO_4^{2-} , BO_3^{3-} , PO_4^{3-} , F^- are tested by their characteristic tests.

8.3 PHYSICAL CHARACTERISTICS

Colour: Many metallic ions and complex ions have colours and consequently their salts are also coloured. Following table gives the expected constituent of the mixture based on its colour.

Table 8.1 Colour of salts

S.No.	Colour	Salt
1.	Black	Oxides: MnO_2 , FeO , CuO , Co_3O_4 , Ni_2O_3 , Fe_3O_4 Sulphides: Ag_2S , CuS , Cu_2S , FeS , CoS , NiS , PbS , HgS , Bi_2S_3 (blackish brown) powdered metals
2.	Blue	Hydrated CuSO_4 , anhydrous CoSO_4
3.	Orange	K_2O_2 , some dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), and ferricyanides, Sb_2S_3
4.	Green	Nickel salts, hydrated ferrous salts, potassium manganate (K_2MnO_4), some copper(II), salts, chromium(III) salts
5.	Brownish yellow	SnS
6.	Dark brown	PbO_2 , Ag_2O , CdO , Fe_2O_3 , CuCrO_4 , FeCl_3 (but yellow in aqueous solution)
7.	Pale brown	MnCO_3
8.	Purple	Potassium permanganates (KMnO_4) and a few Cr(III) salts
9.	Light pink	Hydrated manganese salts
10.	Reddish pink	Hydrated cobalt(II) salts
11.	Red	HgI_2 , Pb_3O_4
12.	Yellow	CdS , PbI_2 , AgBr , AgI , chromates

8.3.1 COLOUR CHANGE ON HEATING

Certain oxides change colour on heating and this fact can be used to identify salt.

Oxides	Colour	
	In cold	On heating
ZnO	white	yellow
SnO_2 , Bi_2O_3	yellow	yellowish brown
Fe_2O_3	brown	black/red
PbO	yellow	

8.3.2 COLOUR OF THE SOLUTION

Colour of the solution	Ions suspected
Yellow	CrO_4^{2-} , Fe^{3+} , $[\text{Fe}(\text{CN})_6]^{4-}$
Green or blue	Cu^{2+} , Ni^{2+} , Fe^{2+} , Cr^{3+}
Pink	Co^{2+} , Mn^{2+}
Orange or purple	Dichromates (orange), permanganates (purple)

Smell: Some salts have their characteristic smell which gives the following information.

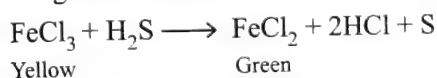
Smell	Conclusion
Vinegar or acetic acid type	Acetates (CH_3COO^-)
Ammoniacal smell	Ammonium salts (NH_4^+)

ILLUSTRATION 8.1

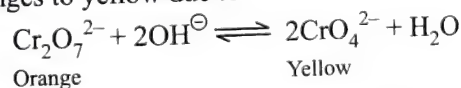
- FeCl_3 is yellow in aqueous solution but on passing H_2S gas, solution turns green. Explain.
- Aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ (orange) changes to yellow. Can you explain?
- Potassium permanganate is purple in colour. On adding KOH , it turns green. What is the compound formed?
- A metallic statue under 'acid-rain' attack turns to bluish-green colour. What can be the probable metal and salt formed?
- Oil paintings turn blackish after some time. What is the salt formed? Assume oil paint contains Pb^{2+} .

Sol.

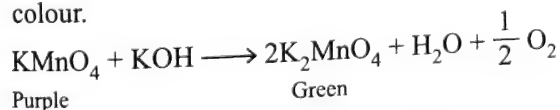
- FeCl_3 is yellow in aqueous solution, but on passing H_2S gas, solution turns green, due to formation of FeCl_2 , which is green in colour.



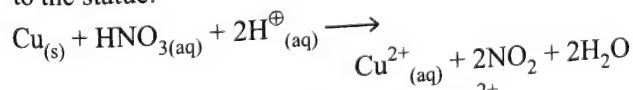
- Aqueous solution of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) changes to yellow due to



- Potassium permanganate, KMnO_4 , reacts with KOH , producing potassium manganate which is green in colour.

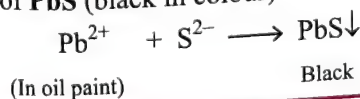


- Acid rain constitutes HNO_3 and H_2SO_4 . HNO_3 on reaction with copper present in statue oxides metallic Cu to Cu^{2+} , which gives a bluish-green colour to the statue.



Hence metal is Cu and salt formed is Cu^{2+} .

- Oil paintings turn blackish after sometime, due to reaction of Pb^{2+} (present in oil paints) with sulphides present in atmosphere, which results in the formations of **PbS** (black in colour)



8.4 ANALYSIS OF ANIONS

Though anion analysis is not systematic as cation analysis, the former may be categorised as:

- First category:** The anions which are decomposed by dil. HCl or H_2SO_4 (5N) are placed in this category. Such anions are CO_3^{2-} , CH_3COO^- , S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ and NO_2^- .
- Second category:** The anions which are decomposed by conc. H_2SO_4 such as Cl^- , Br^- , I^- , NO_3^- and F^- , belong to this category.
- Third category:** The anions which are not covered by the first two categories belong to this category. These are usually detected by precipitation reactions, e.g., SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, PO_4^{3-} and BO_3^{3-} .

An anion may interfere with the detection of another anions, in such cases, special tests known as **combination test** are performed.

Water extracted (W.E.) or sodium carbonate extract (S.C.E.) is used during anion analysis of the mixture.

Preparation of W.E: Small amount ($\approx 40\text{--}50$ mg) of the mixture dissolved in (2–5 mL) of distilled water and boiled for about 1 minute and centrifuge. The centrifugate is called **W. E.**

Preparation of sodium carbonate extract (S.C.E.): To the small amount ($\approx 40\text{--}50$ mg) of the mixture add (≈ 200 mg) of Na_2CO_3 + 5 mL of distilled water and boiled for 5 min and centrifuge. The centrifugate is known as **S.C.E. or S.E.**

Advantages of preparing sodium carbonate extract:

- It affords a convenient method for the preparation of a solution of all the anions of the mixture.
- It helps in the removal of cations which could have interfered in the usual tests of some of the anions by converting them into insoluble carbonates. For example, many anions give characteristic precipitates or colours in almost exactly neutral solution which can easily be obtained when the solution is directly prepared from the mixture and contains basic radicals (other than alkali metal ions) as well.
- The residue obtained in preparation of sodium extract may be dissolved in dil. HCl or conc. HCl and the solution so obtained can be used for identification of cations from group I to group VI.

8.5 ANALYSIS OF FIRST CATEGORY ANIONS

Action of dilute H_2SO_4 : Treat a small amount of mixture with dil. H_2SO_4 . Observe the reaction first in cold and then on gentle heating.

S.No.	Observation	Inference
1.	Colourless and odourless gas is evolved with brisk effervescence in cold	CO_3^{2-} may be present
2.	Light brown coloured, pungent fumes evolved in cold which becomes dense on warming	NO_2^- may be present
3.	Colourless gas is evolved with suffocating odour of burning sulphur	SO_3^{2-} may be present

4.	Colourless gas is evolved with suffocating odour of burning sulphur on heating and solution turns yellow	$\text{S}_2\text{O}_3^{2-}$ may be present
5.	Colourless gas with smell of rotten eggs is evolved; turns filter paper moistened with lead acetate black	S^{2-} may be present
6.	No gas is evolved but the solution smells of vinegar	CH_3COO^- may be present

8.5.1 CONFIRMATORY TESTS FOR ACID RADICALS OR ANIONS

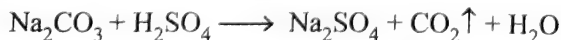
The preliminary tests with dil. H_2SO_4 and conc. H_2SO_4 provide useful information regarding presence of many acid radicals. These are confirmed by at least one distinctive confirmatory test. Some of these confirmatory tests are carried out with solution. It is therefore necessary to have a solution containing all (or most) anions free from heavy metal ions. This is best accomplished by preparing sodium carbonate extract.

8.5.2 CONFIRMATORY TESTS FOR CARBONATE (CO_3^{2-}) ION

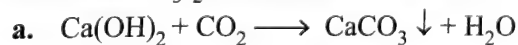
S.No.	Experiment	Observation	Inference
1.	Mixture + few drops of dil. H_2SO_4	Colourless, odourless gas with effervescences in cold, increases on heating	CO_3^{2-} may be present
2. a.	Pass the gas evolved through lime water	Lime water turns milky (CaCO_3)	CO_3^{2-} confirmed
b.	Pass excess of the gas in the lime water	Turbidity disappears giving a clear solution [$\text{Ca}(\text{HCO}_3)_2$]	

8.5.2.1 Chemical Reactions Involved

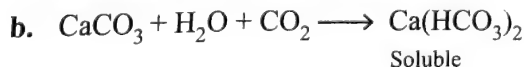
- Carbonate is decomposed by dil. acids ($\text{H}_2\text{SO}_4/\text{HCl}$) to give CO_2 , a colourless and odourless gas. Evolution of CO_2 is the cause of effervescences.



- On passing the gas evolved (CO_2) in the above test through lime-water ($\text{Ca}(\text{OH})_2$), lime water turns milky initially due to the formation of calcium carbonate, CaCO_3 . Excess of CO_2 , when passed through lime water, turbidity disappears and the solution becomes clear due to the conversion of CaCO_3 into $\text{Ca}(\text{HCO}_3)_2$, (calcium bicarbonate).



Lime water Milky



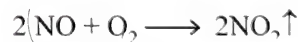
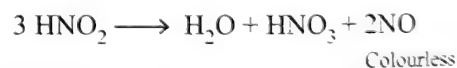
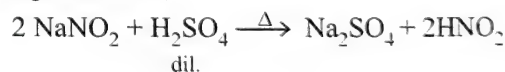
Soluble

8.5.3 TESTS FOR NITRITE (NO_2^-) ION

S.No.	Experiment	Observation	Inference
1.	Mixture + dil. H_2SO_4 . Heat	Light brown pungent fumes are evolved	NO_2^- may be present
2.	Bring a paper dipped in KI and starch solution over the mouth of the test tube	Paper turns bluish violet	NO_2^- confirmed
3.	W.E. + KI solution + starch solution + dil. H_2SO_4	Solution turns blue	NO_2^- confirmed
4.	W.E. + few drops of sulphanilic acid (in CH_3COOH) + few drops of α -naphthylamine (in CH_3COOH)	Red colouration	NO_2^- confirmed
5.	Brown-Ring Test: W.E. + few drops of concentrated soln. of FeSO_4 + a few drops of H_2SO_4 added from the side of test tube.	Brown ring is formed at the junction of two liquids	NO_2^- confirmed

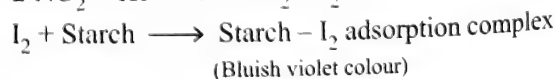
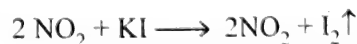
8.5.3.1 Chemical Reactions Involved

- On reaction with dil. acids (H_2SO_4 , HCl , CH_3COOH) a nitrite salt decomposes to give nitric oxide, NO . NO on reaction with atmospheric O_2 forms brown gas NO_2 , (nitrogen dioxide).

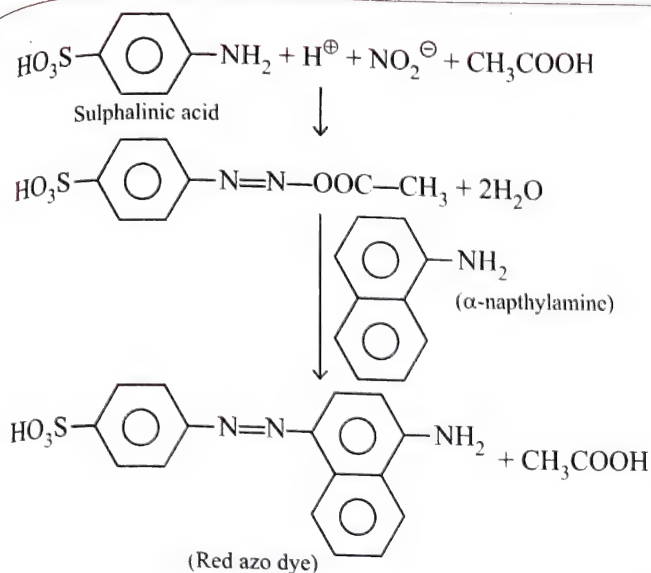


Air Brown gas

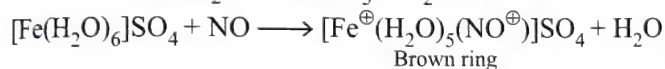
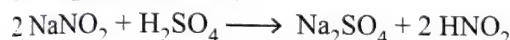
- NO_2 produced in above test, reacts with KI, which results in the liberation of I_2 gas. I_2 on reaction with starch forms starch- I_2 adsorption complex which is bluish violet in colour.



- Same reactions as for test 2.
- Sulphanilic acid and α -naphthylamine are dissolved in separate test tubes in CH_3COOH . These are then added to the water extract, resulting in the formation of red coloured dye.



5. Brown ring test: To the water extract, freshly prepared FeSO_4 solution is added. Dilute H_2SO_4 is added from the side of the test tube, a brown ring is formed at the junction of the two liquids. Brown ring is due to the formation of $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]\text{SO}_4$.



Brown ring complex is paramagnetic with 3 unpaired electrons.

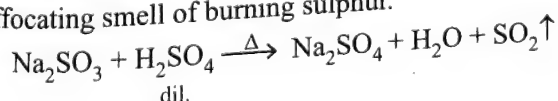
Note: This test should not be performed for nitrate in presence of nitrite, bromide and iodide.

8.5.4 TESTS FOR SULPHITE (SO_3^{2-}) ION

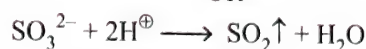
S. No.	Experiment	Observation	Inference
1.	Mixture + few drops of dil. H_2SO_4 . Heat	Colourless gas with pungent and suffocating odour of burning sulphur	SO_3^{2-} may be present
2.	Bring a filter paper moistened with soln of $\text{K}_2\text{Cr}_2\text{O}_7$ acidified with dil. H_2SO_4 over the liberated gas	The colour of the paper turns green	SO_3^{2-} confirmed
3. i.	S.C.E. + dil. HCl (till acidic) + BaCl_2 solution	White ppt. (BaSO_3) which is soluble in conc. HCl	SO_3^{2-} confirmed
ii.	Add Br_2 water to the above solution	White ppt (BaSO_4) insoluble in conc. HCl	SO_3^{2-} confirmed

8.5.4.1 Chemical Reactions Involved

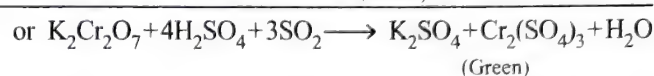
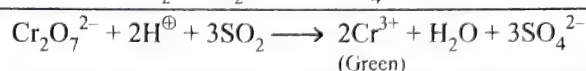
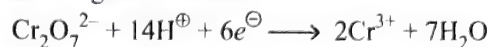
1. Sulphites are decomposed by dilute acids to give sulphur dioxide gas, SO_2 which is a colourless gas with pungent and suffocating smell of burning sulphur.



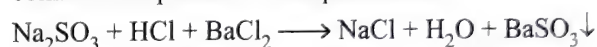
OR



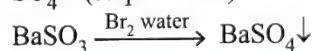
2. $\text{K}_2\text{Cr}_2\text{O}_7$, in acidic medium behaves as an oxidising agent, whereas SO_2 behaves as reducing agent. SO_2 when comes in contact with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ reduces it to $\text{Cr}_2(\text{SO}_4)_3$, which is green in colour.



3. S.C.E. acidified with dil. HCl and then BaCl_2 solution is added, formation of white precipitate soluble in conc. HCl confirms the presence of sulphite ions



On addition of Br_2 water to the above solution, white precipitate of BaSO_4 insoluble in conc. HCl is obtained. Since Br_2 , which is an oxidising agent, oxidises SO_3^{2-} to SO_4^{2-} (sulphate ion).

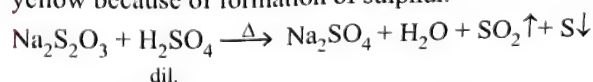


8.5.5 TESTS FOR THIOSULPHATE ($\text{S}_2\text{O}_3^{2-}$) ION

S.No.	Experiment	Observation	Inference
1.	Mixture + dil. H_2SO_4 . Heat	Colourless gas with suffocating odour of burning sulphur. SO_2 is evolved and solution turns yellow (S)	$\text{S}_2\text{O}_3^{2-}$ may be present
2.	Bring a paper moistened with acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$ over the ensuing gas	Colour of the paper turns green	$\text{S}_2\text{O}_3^{2-}$ confirmed
3.	S.C.E. + AgNO_3 solution	White ppt. quickly changing to yellow brown and finally black (Ag_2S)	$\text{S}_2\text{O}_3^{2-}$ confirmed
4.	S.C.E. + few drops of I_2 solution	Colour of I_2 is discharged	$\text{S}_2\text{O}_3^{2-}$ confirmed

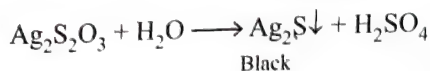
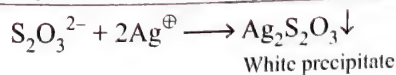
8.5.5.1 Chemical Reactions Involved

1. Thiosulphates are decomposed by dil. acids on heating resulting in the evolution of SO_2 , a colourless gas, with suffocating odour of burning sulphur and solution turns yellow because of formation of sulphur.

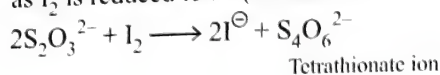


2. Same reaction as for test 2 for sulphite ion.

3. On addition of AgNO_3 solution to S.C.E. a white precipitate ($\text{Ag}_2\text{S}_2\text{O}_3$) is formed which quickly changes to black (Ag_2S)



4. On addition of I_2 solution to S.C.E. colour of I_2 disappears as I_2 is reduced to I^- (iodide ion)

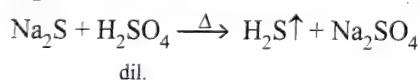


8.5.6 TESTS FOR SULPHIDE (S^{2-}) ION

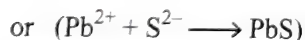
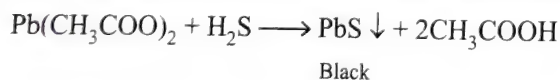
S.No.	Experiment	Observation	Inference
1.	Mixture + few drops of dil. H_2SO_4	Colourless gas with rotten egg smell (H_2S) is evolved on heating	S^{2-} may be present
2.	S.C.E. + dil. H_2SO_4 (to acidify) + lead acetate solution	Black ppt. (PbS)	S^{2-} confirmed
3.	S.C.E. + dil. H_2SO_4 (to acidify) + CdCO_3 solution	Yellow ppt. (CdS)	S^{2-} confirmed
4.	S.C.E. + alkaline solution of sodium nitroprusside	Violet colour	S^{2-} confirmed

8.5.6.1 Chemical Reactions Involved

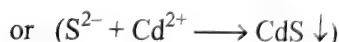
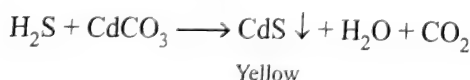
1. Dilute acids decompose sulphide salts on heating to form H_2S gas which is a colourless gas and has rotten egg smell.



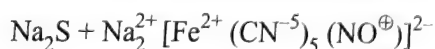
2. Lead acetate, $\text{Pb}(\text{CH}_3\text{COO})_2$ soln. turns black on reacting with H_2S gas due to the formation of lead sulphide,



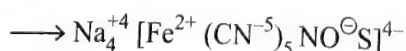
3. Yellow precipitate of CdS is formed when sodium extract reacts with CdCO_3 .



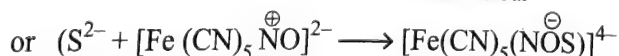
4. On addition to alkaline solution of sodium nitroprusside to S.C.E., violet colouration is obtained.



Sodium nitroprusside



Violet colour

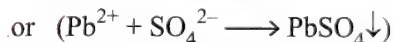
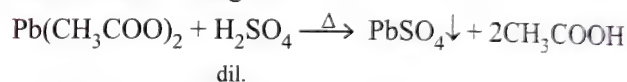


8.5.7 TESTS FOR ACETATE (CH_3COO^-) ION

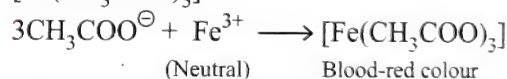
S.No.	Experiment	Observation	Inference
1.	Mixture + few drops of dil. H_2SO_4 . Heat	Smell of vinegar is observed without evolution of any gas	CH_3COO^- may be present
2.	W.E. + neutral FeCl_3 solution	Blood red colouration [$\text{Fe}(\text{CH}_3\text{COO})_3$]	CH_3COO^- confirmed
3.	Mixture + 1 mL $\text{C}_2\text{H}_5\text{OH}$ + 5–6 drops of conc. H_2SO_4 . Warm for about 10 min. Transfer the above solution in a beaker containing about 100 ml of water.	Pleasant fruity odour	CH_3COO^- confirmed

8.5.7.1 Chemical Reactions Involved

1. Dilute acids on reaction with acetates, form acetic acid which has a smell of vinegar.



2. W.E. on reacting with neutral FeCl_3 solution gives blood-red colouration due to formation of ferric acetate. [$\text{Fe}(\text{CH}_3\text{COO})_3$]



Note: In the FeCl_3 test for acetates, the solution must be neutral and must not contain anions which precipitate ferric ions: CO_3^{2-} , SO_3^{2-} , PO_4^{3-} , I^- etc. I^- is oxidised to I_2 by Fe^{3+} ion, which produces a reddish brown colour similar to that expected in the reaction.

3. On treatment of the mixture with ethanol ($\text{C}_2\text{H}_5\text{OH}$) and conc. H_2SO_4 , pleasant fruity smell is obtained due to formation of ethylacetate ($\text{CH}_3\text{COOC}_2\text{H}_5$)

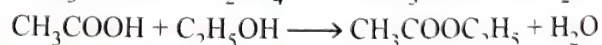


ILLUSTRATION 8.2

- a. Identify (A), (B) and (C).

$\text{A} + \text{dil. H}_2\text{SO}_4 \longrightarrow$ brown colour vapours turning (KI + starch) paper blue.



(A) $\xrightarrow{\Delta}$ (B) (gas) + (C) (gas, but liquid at room temperature)

- b. CO_2 and SO_2 both turn lime water milky. How will you detect the presence if both are present in a mixture?

- c. (A), ($\text{M}_2\text{X} \cdot 7\text{H}_2\text{O}$) has water and M_2X (M is monovalent alkaline cation, and X is any divalent anion) in 1:1 ratio by weight. (A) on reaction with dil. H_2SO_4 gives a gas that turns $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ solution green. Identify (A) and explain reactions.

d. (A), (Black) + dil. $\text{H}_2\text{SO}_4 \longrightarrow$ (B) (gas) + (C) (light green colour solution). Gas (B) turns lead acetate paper black. What are (A), (B) and (C)?

Sol. a. (A): NH_4NO_2 (B): N_2 (C): H_2O

b. Pass the mixture of gases first into acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution then into lime water.

If $\text{K}_2\text{Cr}_2\text{O}_7$ solution turns green – SO_2

If lime water turns milk – CO_2

c. (A): $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$

d. (A): FeS (B): H_2S (C): FeSO_4

8.6 ANALYSIS OF SECOND CATEGORY ANIONS

Action of conc. H_2SO_4 : Treat a small amount of mixture with conc. H_2SO_4 . Observe the reaction first in cold and then on gentle heating.

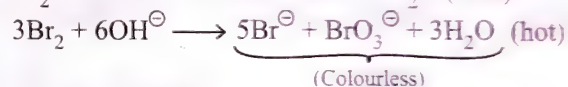
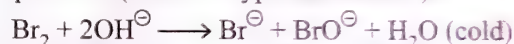
S.No.	Observation	Inference
1.	Colourless gas with pungent odour is evolved; gives white fumes when a glass rod dipped in NH_4OH is brought over it	Cl^\ominus may be present
2.	Evolution of light reddish brown coloured gas with a pungent odour; gives a fumes when a rod dipped in NH_4OH is brought over it	Br^\ominus may be present
3.	Evolution of violet fumes with pungent odour	I^\ominus may be present
4.	Light brown coloured gas with pungent odour is evolved, colour deepens on addition of Cu turnings	NO_3^\ominus may be present
5.	Colourless, odourless gas is evolved, turns lime-water milky	$\text{C}_2\text{O}_4^{2-}$ may be present

8.6.1 TESTS FOR CHLORIDE (Cl^\ominus) ION

S.No.	Experiment	Observation	Inference
1.	Mixture + few drops of conc. H_2SO_4 . Heat	Colourless gas with pungent smell (HCl)	Cl^\ominus may be present
2. i.	Bring a glass rod dipped in NH_4OH near the mouth of the test tube	White dense fumes are formed	Cl^\ominus may be present
ii.	Add MnO_2 in the same test tube	Pale green gas (Cl_2)	
3.	S.C.E. and heat + dil. HNO_3 (to acidity) + AgNO_3 solution	White ppt. soluble in NH_4OH . White ppt. reappears on adding dil. HNO_3	Cl^\ominus confirmed
4.	Chromylchloride test		

i.	In a dry test tube, take the mixture + $\text{K}_2\text{Cr}_2\text{O}_7$ solid (twice the amount of mixture + conc. H_2SO_4 . Heat	Deep orange red vapours of chromyl chloride (CrO_2Cl_2)	
ii.	Pass the vapours from (i) in 5% NaOH solution in a test tube	Colour of NaOH solution changes to yellow	
iii.	Yellow solution from (i) + CH_3COOH dropwise till acidic + lead acetate solution	Yellow precipitate	Cl^\ominus confirmed

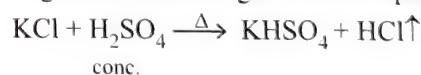
Note: 1. Bromides and iodides do not interfere with the chromyl chloride (CrO_2Cl_2) test, because they are oxidised to Br_2 (red vapours) and I_2 (violet vapours) which dissolve in the NaOH solution to form colourless products (halide + hypohalite/halate).



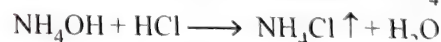
2. Hg_2Cl_2 and HgCl_2 do not respond to the chromyl chloride test because they are ionised to a very small extent. This test fails in case of chlorides of Pb, Ag, Sb and Sn only partially form CrO_2Cl_2 in the reaction.

8.6.1.1 Chemical Reactions Involved

1. On heating with conc. H_2SO_4 , a chloride salt is decomposed to give a colourless gas HCl with pungent smell.



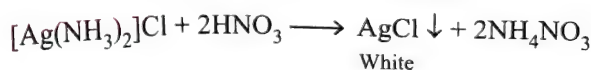
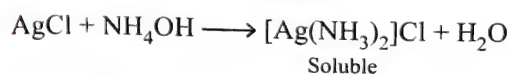
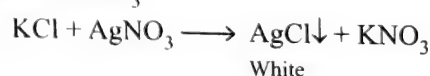
2. a. HCl gas evolved in the above step, when comes in contact with NH_4OH , results in the formation of dense white fumes due to formation of NH_4Cl



b. (MnO_2) manganese dioxide oxidises HCl to Cl_2 , a pale green gas.

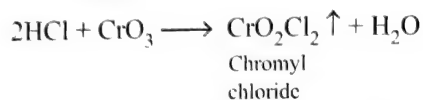
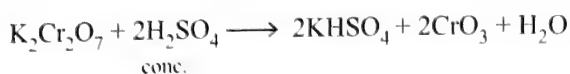
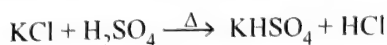


3. On addition of AgNO_3 solution, to the chloride salt, a white precipitate of AgCl is formed. AgCl is soluble in NH_4OH due to formation of complex $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$, which decomposes on addition of HNO_3 .

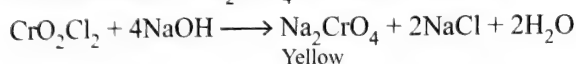


4. Chromylchloride test (not for Br^- / I^- ions)

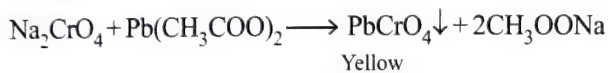
- a. On addition of conc. H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ (potassium dichromate) to chloride salt, deep orange red vapours of chromyl chloride, CrO_2Cl_2 , are produced.



- b. Colour of NaOH solution changes to yellow, when chromyl chloride vapours are passed through it due to the formation of Na_2CrO_4 (sodium chromate).



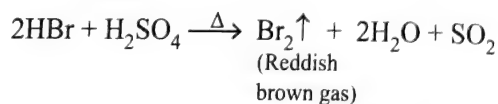
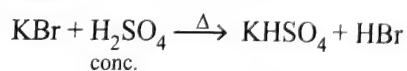
- c. On addition of lead acetate, $\text{Pb}(\text{CH}_3\text{COO})_2$ to the above solution, yellow precipitate of PbCrO_4 (lead chromate) is formed.

**8.6.2 TESTS FOR BROMIDE (Br^-) ION**

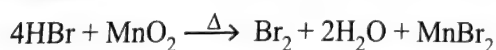
S.No.	Experiment	Observation	Inference
1.	Mixture + few drops of conc. H_2SO_4 . Heat	Reddish brown pungent gas (Br_2) is evolved	Br^- may be present
2.	In the above solution add MnO_2 solid. Heat	Gas becomes denser	Br^- may be present
3.	S.E. + dil. HNO_3 (to acidify) + AgNO_3 solution	Light yellow precipitate sparingly soluble in NH_4OH (dil.) but soluble in conc. NH_3	Br^- confirmed
4.	Layer test: S.E. + $\text{CCl}_4 / \text{CHCl}_3 + \text{Cl}_2$ water. Shake vigorously	The organic solvent layer turns brown	Br^- confirmed

8.6.2.1 Chemical Reactions Involved

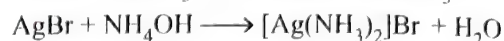
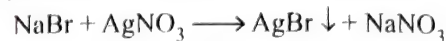
1. On heating bromide salt on reaction with conc. H_2SO_4 is decomposed to give a reddish brown gas (Br_2) with pungent smell.



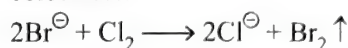
2. Addition of MnO_2 to the above solution results in oxidation of HBr to Br_2 , resulting in intensification of reddish brown fumes.



3. Addition of AgNO_3 solution to the acidified sodium carbonate extract results in formation of light yellow precipitate of AgBr which is sparingly soluble in NH_4OH .



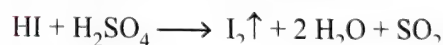
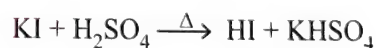
4. **Layer test:** Bromine (Br_2) is liberated from bromide salt on addition of an oxidising agent (Cl_2 water/drop of KMnO_4 solution/conc. HNO_3). Br_2 being more soluble in organic medium ($\text{CCl}_4 / \text{CHCl}_3$) gives an orange brown colour to the lower organic layer and the upper aqueous layer remains colourless.

**8.6.3 TESTS FOR IODIDE (I^-) ION**

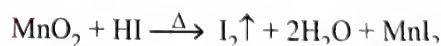
S.No.	Experiment	Observation	Inference
1.	Mixture + few drops of conc. H_2SO_4 . Heat	Violet coloured pungent fumes are evolved	I^- may be present
2.	Above solution + MnO_2 (s). Heat	Fumes becomes denser	I^- may be present
3.	S.E. + dil. HNO_3 (till acidic) + AgNO_3 solution	Yellow precipitate insoluble in NH_4OH	I^- confirmed
4. i.	Layer test: S.E. + CCl_4 (or CHCl_3 or CS_2) + Cl_2 water. Shake vigorously	Organic solvent layer turns violet	I^- confirmed
ii.	In the solution (4) add excess of Cl_2 water	Organic solvent layer becomes colourless	I^- confirmed

8.6.3.1 Chemical Reactions Involved

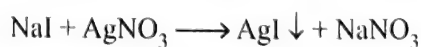
1. Iodides are decomposed by conc. H_2SO_4 on heating to liberate violet fumes.



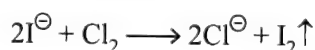
2. On addition of MnO_2 , to the above mixture, only I_2 is evolved.



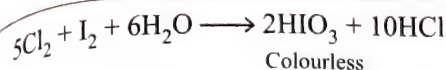
3. Addition of AgNO_3 solution to the acidified sodium carbonate results in the formation of yellow precipitate (AgI), which is insoluble in NH_4OH .



4. **Layer test:** Addition of Cl_2 water, an oxidising agent to the sodium extract, results in the liberation of I_2 from iodide, which gives violet colour to the organic layer. On excess addition of Cl_2 water, the organic layer becomes colourless due formation of iodic acid, HIO_3



Violet



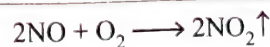
8.6.4 TESTS FOR NITRATE (NO_3^-) ION

S.No.	Experiment	Observation	Inference
1.	Mixture + few drops of conc. H_2SO_4	Reddish brown fumes (NO_2) with pungent odour are evolved	NO_3^- may be present
2.	Mixture (i) + Cu turnings. Heat	Fumes becomes denser	NO_3^- may be present
3.	Ring test: S.E. + dil. HCl (till acidic) + freshly prepared solution of FeSO_4 + few drops of conc. H_2SO_4 gradually from the side of the test tube without disturbing the liquids in the test tube.	Brown ring is formed at the junction of the two liquids	NO_3^- confirmed

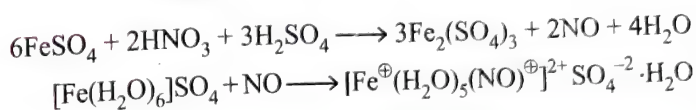
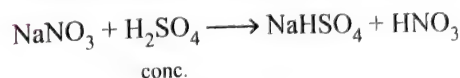
Note: Bromide and iodides interfere in this test because of liberated halogens. Nitrites give similar test as nitrates.

4.	S.E. + a piece of Zn metal + dil. H_2SO_4 . Boil for 5 min. Add few drops each of KI and starch solution	Violet colouration	NO_3^- confirmed
5.	Dye test: S.E. + CH_3COOH till acidic + few drops of sulphanilic acid + few drops of α -naphthyl amine + Zn dust (in CH_3COOH)	Red colouration	NO_3^- confirmed

Note: Nitrites give similar test but without adding Zn dust.



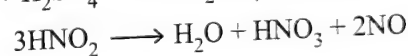
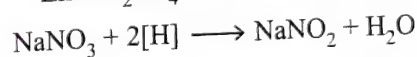
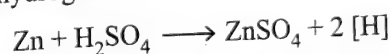
- 3. Ring test:** This test is carried out by the addition of freshly prepared solution of FeSO_4 to the nitrate solution, followed by slow addition of conc. H_2SO_4 from the side of the test tube so that the acid forms a layer beneath the mixture. A brown ring will be formed where the liquids meet or at the junction of the two liquids. Brown ring is formed due to the complex $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]\text{SO}_4$



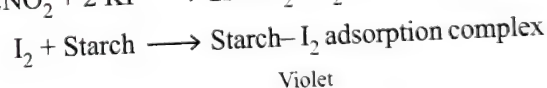
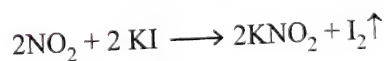
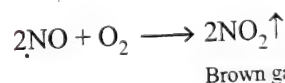
Brown ring

The brown complex contains 3 unpaired electrons and is paramagnetic with $\mu = \sqrt{3(3+2)} = \sqrt{15}$ B.M.

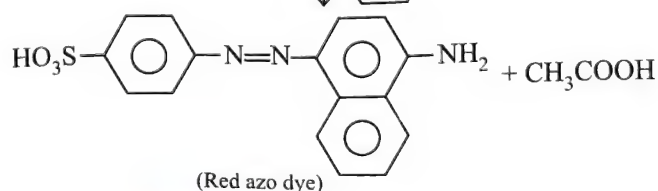
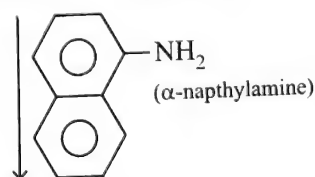
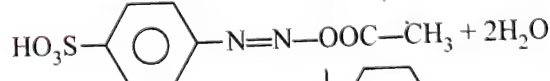
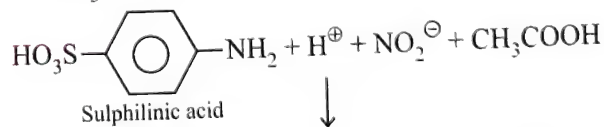
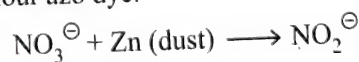
- 4.** Boil S.E. with Zn dust and dil. H_2SO_4 . Add KI and starch solution, violet colouration is observed. Zinc dust in presence of H_2SO_4 acts as reducing agent, by liberating nascent hydrogen. Nitrates are being reduced to nitrite.



Colourless

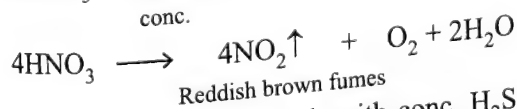
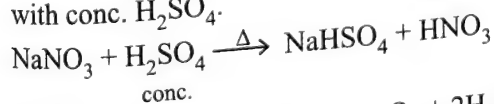


- 5. Dye test:** To the nitrates, α -naphthylamine solution (in CH_3COOH), sulphanilic acid (in CH_3COOH) and zinc dust are added. Red coloured solution is obtained. Zinc dust reduces nitrates to nitrites, which further reacts to form red colour azo dye.

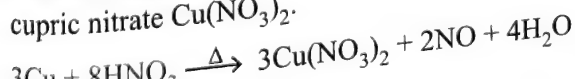


8.6.4.1 Chemical Reactions Involved

1. Reddish brown vapours of nitrogen dioxide (NO_2) accompanied by pungent acid vapours of nitric acid (HNO_3), which fumes in the air, are formed on heating nitrate salt with conc. H_2SO_4 .



2. On heating the nitrate salt with conc. H_2SO_4 and copper turnings, reddish brown fumes become denser and the solution acquires a blue colour due to the production of cupric nitrate $\text{Cu}(\text{NO}_3)_2$.

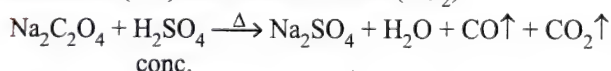


8.6.5 TESTS FOR OXALATE ($C_2O_4^{2-}$) ION

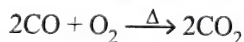
S.No.	Experiment	Observation	Inference
1.	Mixture + conc. H_2SO_4 . Heat	Colourless, odourless gas evolved	
2.	Bring the mouth of the test tube near the flame and take it off	The gas burns with a blue flame at the mouth of the test tube	$C_2O_4^{2-}$ may be present
3.	Mixture + dil. H_2SO_4 . Heat till the effervescences (if any) ceases. Add a pinch of $MnO_2(s)$	Brisk effervescence (CO_2) is observed	$C_2O_4^{2-}$ confirmed
4. i.	CaCl₂ test: S.E. + CH_3COOH (till acidic) + $CaCl_2$ solution	White ppt. soluble in dil. H_2SO_4	$C_2O_4^{2-}$ confirmed
ii.	In the above solution add dil. H_2SO_4 and few drops of $KMnO_4$ solution	Colour of $KMnO_4$ is discharged	$C_2O_4^{2-}$ confirmed

8.6.5.1 Chemical Reactions Involved

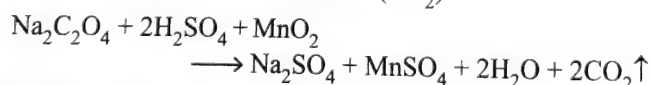
1. Oxalate salts are decomposed by conc. H_2SO_4 to give carbon monoxide (CO) and carbon dioxide (CO_2).



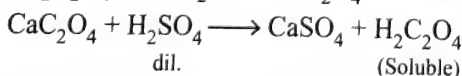
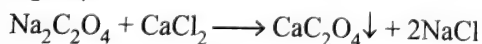
2. The gas evolved (CO) burns with a blue flame at the mouth of the test tube.



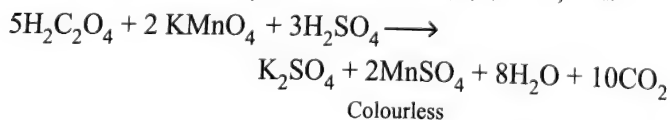
3. Addition of MnO_2 to mixture and dil. H_2SO_4 , results in evolution of brisk effervescences (CO_2).



4. **CaCl₂ test:** Oxalates react with $CaCl_2$ solution to give white ppt. of calcium oxalate (CaC_2O_4) which is soluble in dil. H_2SO_4 .



5. To the above solution dil. H_2SO_4 and $KMnO_4$ solution are added. Colour of $KMnO_4$ is discharged as oxalates reduce permanganate (MnO_4^-) to manganese(II) (Mn^{2+}) ion.



or

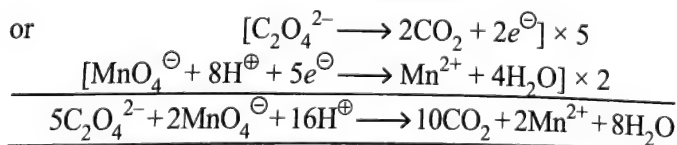


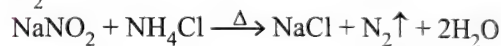
ILLUSTRATION 8.3

- Arrange AgF , $AgCl$, $AgBr$ and AgI in the increasing order of solubility in water.
- NO_2^- interferes in the 'Ring Test' of NO_3^- . Suggest a chemical method of removal of NO_2^- .
- While testing oxalate, gas obtained burns with a blue flame initially but is put off instantly even as gas appears coming. Explain.
- I^- also interferes in the 'Ring Test' of NO_3^- . Suggest a chemical reagent that can remove I^- .
- Colourless solid (A) $\xrightarrow{\Delta}$ (B) gas + (C) gas. Aqueous solutions of (A) and (B) turn blue litmus red while that of (C) turns red litmus blue. Aqueous solutions of (A) and (B) also give white ppt. with $AgNO_3$ solution soluble in aqueous solution of (C). Identify (A), (B) and (C).
- Can you detect Br^- and I^- by 'Layer Test' if present together?

Sol.

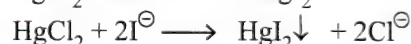
- a. $AgI < AgBr < AgCl < AgF$

- b. Boil the mixture with NH_4Cl , NO_2^- is decomposed as N_2 :



- c. $H_2C_2O_4 \xrightarrow{\Delta} H_2O_{(l)} + CO_{(g)} + CO_{2(g)}$

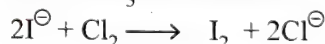
- d. $HgCl_2$ removes I^- as HgI_2



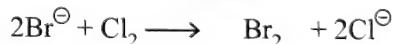
Orange ppt

- e. (A): NH_4Cl (B): HCl (C): NH_3

- f. Reducing power $I^- > Br^- > Cl^- > F^-$. Add Cl_2 water and $CHCl_3$ into mixture of I^- and Br^-



Violet



Orange yellow

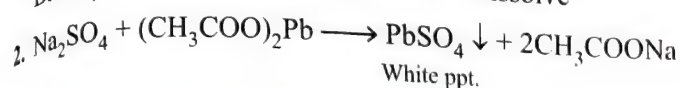
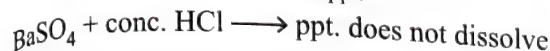
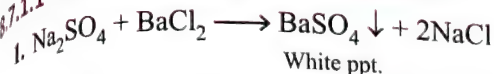
Br_2 will also oxidise I^- to I_2 . Thus, first there will be violet colour in $CHCl_3$ layer. Extract aq. layer (containing Br^-) and repeat adding Cl_2 water and $CHCl_3$. Orange-yellow colour in $CHCl_3$ layer confirms Br^- .

8.7 ANALYSIS OF THIRD CATEGORY ANIONS

8.7.1 TESTS FOR SULPHATE (SO_4^{2-}) ION

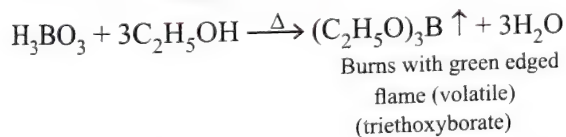
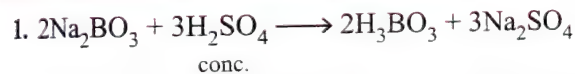
S.No.	Experiment	Observation	Inference
1. i.	S.C.E. + dil. HCl (till acidic) + $BaCl_2$ solution	Curdy white ppt.	SO_4^{2-} may be present
ii.	White ppt (1) + conc. HCl or conc. HNO_3	The ppt. does not dissolve	SO_4^{2-} confirmed
2.	S.C.E. + CH_3COOH (till acidic) + lead acetate solution	White ppt.	SO_4^{2-} confirmed

8.7.1.1 Chemical Reactions Involved

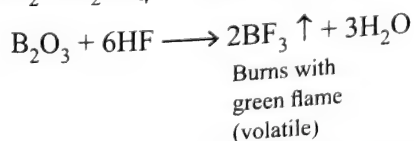
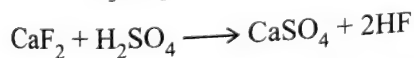
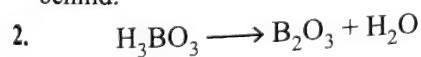
8.7.2 TESTS FOR BORATE (BO_3^{3-}) ION

S.No.	Experiment	Observation	Inference
1.	In a boiling tube, fitted with cork and glass tube take mixture. Add 1 mL conc. H_2SO_4 and 4-5 mL of ethyl or methyl alcohol warm and burn the ensuing gas in the flame.	The gas ($\text{C}_2\text{H}_5\text{O})_3\text{B}$ burn with green edged flame	BO_3^{3-} confirmed
2.	Mixture + powdered CaF_2 + little of conc H_2SO_4 to make a paste. Bring this paste, on the end of glass rod, near the edge of flame without touching it.	Colours the flame green	BO_3^{3-} confirmed

8.7.2.1 Chemical Reactions Involved



This test is performed in test tube and not in china dish, as Cu and Ba both respond to this test. In this way, only vapours of triethoxyborate are able to reach the mouth of the test tube and gives green edged flame, whereas Cu and Ba are left behind.



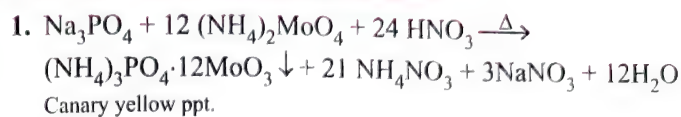
This test is quite reliable, as Cu and Ba do not interfere.

8.7.3 TESTS FOR PHOSPHATE (PO_4^{3-}) ION

S.No.	Experiment	Observation	Inference
1.	Mixture + conc. HNO_3 . Boil and cool. Add ammonium molybdate solution in excess, boil and cool.	Canary yellow ppt. Insoluble in $\text{NH}_4\text{OH}/\text{NaOH}$	PO_4^{3-} confirmed

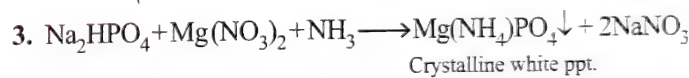
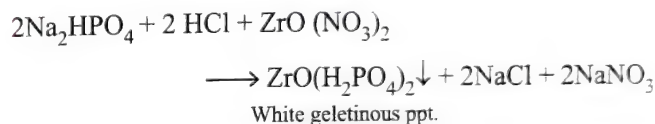
2.	S.E. + dil. HCl till acidic (~1N HCl) + Zirconyl nitrate reagent	White gelatinous ppt. of zirconyl phosphate	PO_4^{3-} confirmed
3.	S.E. + Magnesium nitrate reagent	Crystalline white ppt.	PO_4^{3-} confirmed

8.7.3.1 Chemical Reactions Involved



i. Arsenates give a similar test on boiling. If As is present then test for PO_4^{3-} with filtrate of group II.

ii. Reducing agents such as S^{2-} , SO_3^{2-} affect the reaction as they produce 'molybdenum blue' ($\text{MoO}_8 \cdot x\text{H}_2\text{O}$). The solution therefore turns blue and should be destroyed before carrying out this test and hence the mixture is first boiled with conc. HNO_3 , an oxidising agent.



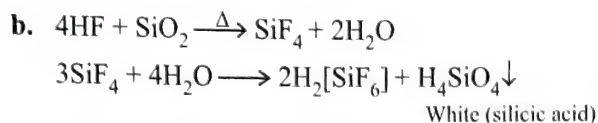
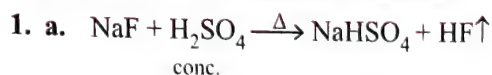
Magnesium nitrate reagent is a solution containing magnesium nitrate $\text{Mg}(\text{NO}_3)_2$, ammonium nitrate (NH_4NO_3) and a little aqueous NH_3 .

On treatment with magnesium nitrate reagent white crystalline ppt. of $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (magnesium ammonium phosphate) is produced.

8.7.4 TESTS FOR FLUORIDE (F^-) ION

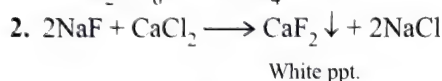
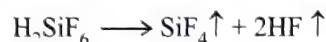
S.No.	Experiment	Observation	Inference
1. i.	Mixture + conc. H_2SO_4 . Heat.	Colourless gas (HF) is evolved which fumes in moisture and test tube acquires a greasy appearance	F^- may be present
ii.	In above solution add sand. Heat. Bring a glass rod moistened with water near the mouth of the test tube	White waxy deposit (H_4SiO_4) on the moist part of glass rod	F^- confirmed
2. i.	S.E. + CH_3COOH (till acidic) + CaCl_2 solution	White ppt. insoluble in dil. H_2SO_4	F^- confirmed
ii.	Above ppt. + dil. H_2SO_4 + few drops of KMnO_4 solution	The colour of KMnO_4 is not discharged	F^- confirmed

8.7.4.1 Chemical Reactions Involved



HF gas being corrosive, attacks silica present in the glass test tube to produce oily drops. The corrosive action of HF is also responsible for the greasy appearance.

Fluorosilicic acid [$\text{H}_2(\text{SiF}_6)$], which is known only in aqueous solution, is decomposed into silicon tetrafluoride and hydrofluoric acid on evaporating the aqueous solution.



CaF_2 is insoluble in dil. H_2SO_4 and does not react with KMnO_4 and hence colour of KMnO_4 is not discharged.

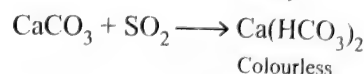
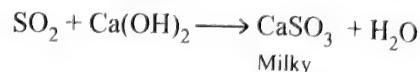
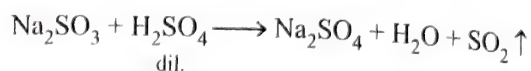
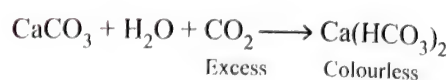
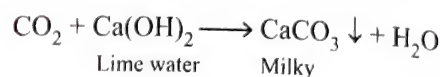
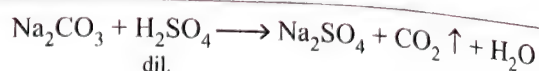
8.8 SPECIFIC TESTS FOR COMBINATIONS OF ACID RADICALS

Many times, while performing the test for the presence of a particular anion in the given mixture, the presence of some other anions may cause interference in the usual tests for the radical. In such cases special tests are performed or usual tests are modified in order to detect such radicals simultaneously and conveniently. Some such cases are discussed below.

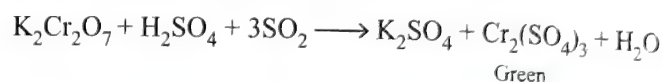
8.8.1 CARBONATE (CO_3^{2-}) AND SULPHITE (SO_3^{2-})

Carbonates and sulphites decompose on treatment with dil. H_2SO_4 to give CO_2 and SO_2 gases respectively, both of which turn lime water milky. The dichromate test for SO_3^{2-} however is not influenced by CO_3^{2-} . Hence SO_3^{2-} interfere with the test for CO_3^{2-} but CO_3^{2-} does not interfere with the test for sulphite. To test for the presence of carbonate and sulphite in a mixture the following test is performed:

Experiment	Observation	Inference
Take the mixture and small amount of powdered $\text{K}_2\text{Cr}_2\text{O}_7$ in a test tube. Add a little of dil. H_2SO_4 and warm. Pass the gas evolved through lime water	i. If the contents of test tube becomes green and lime water turns milky	SO_3^{2-} as well as CO_3^{2-} are present
	ii. If the contents of test tube remains unchanged and lime water turns milky	Only CO_3^{2-} is present
	iii. If the contents of test tube becomes green and lime water remains unchanged	Only SO_3^{2-} is present.



In presence of $\text{K}_2\text{Cr}_2\text{O}_7$, SO_3^{2-} ions which produce SO_2 reacts with $\text{K}_2\text{Cr}_2\text{O}_7$ to give green coloured compound, whereas CO_2 does not react with $\text{K}_2\text{Cr}_2\text{O}_7$.



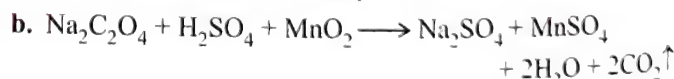
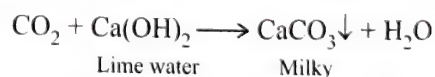
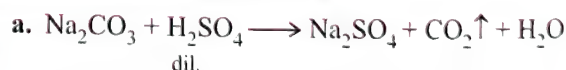
8.8.2 CARBONATE (CO_3^{2-}) AND OXALATE ($\text{C}_2\text{O}_4^{2-}$)

Carbonates are decomposed by both dil. and conc. H_2SO_4 , whereas oxalates are decomposed by conc. H_2SO_4 only to give CO_2 . Carbonate interferes in this test for oxalates. However CO_3^{2-} does not interfere with CaCl_2 for $\text{C}_2\text{O}_4^{2-}$.

$\text{CO}_3^{2-} \longrightarrow$ Lime water test.

$\text{C}_2\text{O}_4^{2-} \longrightarrow$ CaCl_2 test. (Already discussed in tests for oxalate ion) An alternate method may be employed to test for carbonate and oxalate in a mixture:

S.No.	Experiment	Observation	Inference
1.	Heat the mixture with dil. H_2SO_4 and pass the gas through lime water	Lime-water turns milky	CO_3^{2-} present
2.	Heat till effervescence ceases. Add a pinch of MnO_2 solid	Fresh effervescence is observed	$\text{C}_2\text{O}_4^{2-}$ present

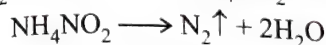


8.8.3 NITRITE (NO_2^-) AND NITRATE (NO_3^-)

NO_2^- can be detected in presence of NO_3^- by treatment with dil. H_2SO_4 , KI-starch test or by ring test or α -naphthyl amine, sulphanilic acid test. However NO_3^- cannot be detected in the presence of NO_2^- , because it gives all the test of NO_2^- . NO_2^- and NO_3^- in a mixture can be detected as follows:

Nitrite is completely decomposed by one of the following methods:

a. Boiling W.E./S.E. with solid NH_4Cl added in pinches till effervescence ceases.



b. Boiling with dil. H_2SO_4 and solid urea in pinches till effervescence ceases.

c. Adding little sulphanilic acid to a solution or S.E. The last named is most efficient. NO_3^- is now tested using this solution by using ring test or converting NO_3^- to NO_2^- by adding Zn dust and dil. H_2SO_4 and testing for NO_2^- ion.

8.8.4 NITRATE (NO_3^-), BROMIDE (Br^-) AND IODIDE (I^-)

All are decomposed by conc. H_2SO_4 to give NO_2 , Br_2 , I_2 respectively. Whereas NO_2 and Br_2 are brown, I_2 is violet in colour. The brown ring test for NO_3^- cannot be applied effectively because Br_2 and I_2 evolved obscure the brown ring due to NO_3^- . Therefore they are detected in the mixture as follows:

a. Br^- and I^- can be detected by layer test, NO_3^- does not interfere. Nitrate is converted to NO_2^- by treatment with Zn metal and conc. H_2SO_4 , and then NO_2^- is detected by usual test. If I^- is present, the colour of the solution will turn blue violet on adding starch solution without adding KI solution.

b. Remove halides by adding a saturated solution of ammoniacal silver sulphate solution $[\text{Ag}(\text{NH}_3)_2]_2\text{SO}_4$ (prepared by dissolving 7.8 g of pure silver sulphate in 25 mL of 4N NH_4OH and diluting to 100 mL with water). A precipitate of AgBr or AgI will be formed. Filter the precipitate and test for NO_3^- in the filtrate.

8.8.5 CHLORIDE (Cl^-), BROMIDE (Br^-) AND IODIDE (I^-)

Chlorides, bromides and iodides are all decomposed by conc. H_2SO_4 producing HCl , HBr + Br_2 and I_2 respectively. When any two or all the three are present in the mixture, the characterisation of evolved gases is not possible because their colours and smells may be intermixing. All these anions give precipitate with AgNO_3 in solution. Hence this test also will not give characteristic and distinctive result. Following tests can be carried out to detect all the three in the mixture.

1. The presence of Cl^- can be confirmed by chromylchloride test (Br^- and I^- do not give similar tests). Br^- and I^- are detected by layer test (Cl^- does not interfere).

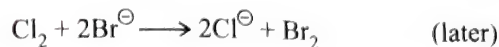
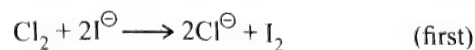
2. **Layer test for Br^- and I^- :** S.C.E. + $\text{CCl}_4/\text{CS}_2/\text{CHCl}_3$ + Cl_2 water. Shake the contents vigorously. Following changes may take place.

a. **Organic layer remains colourless:** Both Br^- and I^- are absent.

b. Organic layer turns violet, this shows the presence of I^- . Add excess of Cl_2 water. Organic layer becomes colourless. Only I^- is present.

c. If organic layer first turns violet, then brown on excess addition of Cl_2 water. Both I^- and Br^- are present.

d. If organic layer turns brown in colour. Only Br^- is present. This test is based on the easier replacement of I^- from a salt than that of Br^- from its salt by chlorine.



Reduction potential of $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

Hence Cl_2 can oxidise I^- to I_2 faster than Br^- to Br_2 .

8.8.6 NITRATE (NO_3^-) AND BROMIDE (Br^-)

Nitrates and bromides are decomposed by conc. H_2SO_4 producing NO_2 and Br_2 gases respectively, both of which are brownish in colour and turn KI-starch paper blue in colour. These are detected in a mixture as follows.

Br^- can be tested by layer test or AgNO_3 test (NO_3^- does not interfere). NO_3^- is detected by converting it into NO_2^- by adding a zinc dust and small amount of dil. H_2SO_4 to a portion of S.E. and boiling for some time and perform the test for NO_2^- ion.

8.8.7 NITRATE (NO_3^-) AND IODIDE (I^-)

The conc. H_2SO_4 test is not disinctive for these two anions when present together in a mixture because they evolve NO_2 and I_2 gases which are brown and violet respectively. These anions can be detected and confirmed by the following test:

I^- — layer test or AgNO_3 test

NO_3^- — Convert to NO_2^- by adding dil. H_2SO_4

+ Zn dust and then apply tests for NO_2^-

8.8.8 FLUORIDE (F^-) AND OXALATE ($\text{C}_2\text{O}_4^{2-}$)

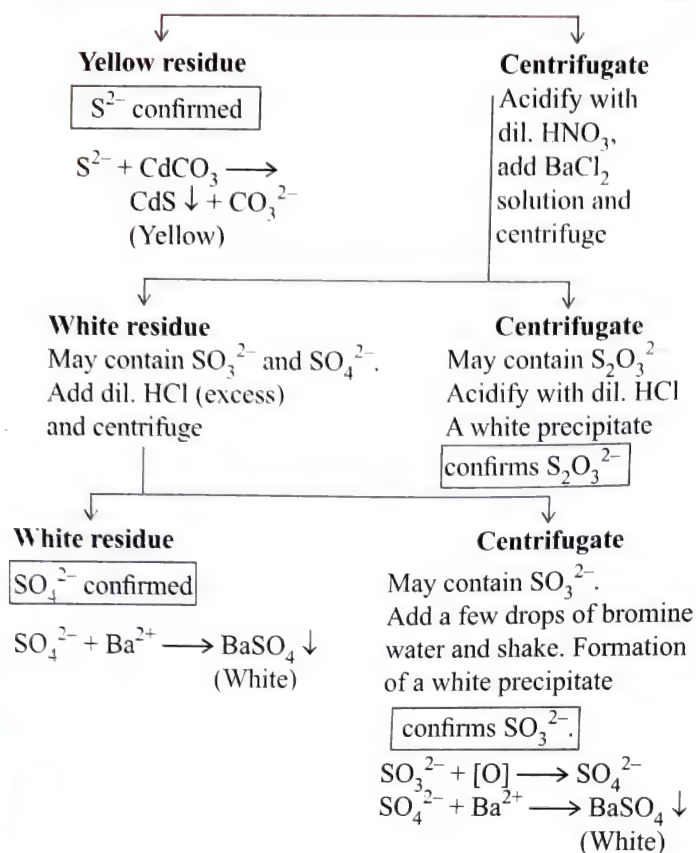
Fluoride and oxalate are rarely given simultaneously in the mixture. They give white ppt. of CaF_2 and CaC_2O_4 when CaCl_2 solution is added to their acidic solution (S.C.E. acidified with CH_3COOH). These precipitates are distinguished as follows.

Treat the ppt. with dil. H_2SO_4 . CaC_2O_4 dissolves whereas CaF_2 is insoluble.

1.	S.E. + dil. CH_3COOH (till acidic) + CaCl_2 solution	White ppt. ($\text{CaF}_2/\text{CaC}_2\text{O}_4$)	
2.	Dissolve the ppt. in dil. H_2SO_4	Filtrate (CaC_2O_4) Residue (CaF_2)	
3.	Filtrate + dil. KMnO_4	Colour of KMnO_4 is discharged	$\text{C}_2\text{O}_4^{2-}$ confirmed
4.	Residue + dil. H_2SO_4 + KMnO_4 solution	Colour of KMnO_4 is not discharged	F^- confirmed

8.8.9 SULPHIDE (S^{2-}), SULPHITE (SO_3^{2-}), THIOSULPHATE ($\text{S}_2\text{O}_3^{2-}$) AND SULPHATE (SO_4^{2-})

Take 10 drops S.C.E. and shake it in 10 mg of CdCO_3 . Heat for 1 min and centrifuge.



8.8.10 PHOSPHATE (PO_4^{3-}) AND ARSENATE (AsO_4^{3-})

The salts of arsenic are converted to arsenates when boiled with conc. HNO_3 . Thus when a mixture containing arsenic and phosphate is tested for the presence of PO_4^{3-} by adding conc. HNO_3 and ammonium molybdate solution, arsenic is also precipitated as ammonium arsenate along with ammonium phosphomolybdate; both of which are yellow in colour. However zirconyl nitrate test for PO_4^{3-} is not influenced by As^{3+} . When As^{3+} is present in a mixture containing PO_4^{3-} , PO_4^{3-} is tested in the filtrate of group II after removal of As^{3+} as As_2S_3 .

ILLUSTRATION 8.4

a. $(A) + KBr \rightarrow$ yellow ppt. (B)

$(A) + \text{conc. } H_2SO_4 \xrightarrow{\Delta}$ brown vapours intensified with Cu-turnings.

(B) dissolves in hypo forming a soluble complex (C). What are (A), (B) and (C) and explain their reactions?

b. SO_3^{2-} and SO_4^{2-} both give white ppt. with $BaCl_2$ solution. How is SO_3^{2-} detected in presence of SO_4^{2-} ?

c. $Na_2B_4O_7 \cdot 10H_2O + \text{conc. } H_2SO_4 \xrightarrow{\Delta} (A) \xrightarrow{CH_3OH, \Delta} (B)$. Identify (A) and (B).

d. $(A) + \text{dil. } H_2SO_4 \xrightarrow{\Delta}$ gas (B).

Gas (B) turns $K_2Cr_2O_7/H^+$ solution green. Aq. solution of $(A) + BaCl_2 \rightarrow$ white ppt. (C).

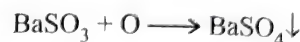
Filtrate after removing (C) + Br_2 water \rightarrow white ppt. (C). Identify (A), (B) and (C).

e. SO_4^{2-} also gives white ppt. with lead acetate but ppt. dissolves in ammonium acetate solution. Explain.

Sol.

a. (A): $AgNO_3$ (B): $AgBr$ (C): $Na_3[Ag(S_2O_3)_2]$

b. $BaSO_4$ is insoluble in conc. HCl , while $BaSO_3$ remains soluble. Separate $BaSO_4$ and add Br_2 water into filtrate. SO_3^{2-} is oxidised to SO_4^{2-} and gives white ppt. of $BaSO_4$.

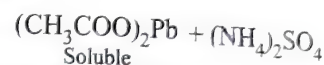


c. (A): H_3BO_3

(B): $(CH_3O)_3B$, burns with green edged flame.

d. (A): $SO_3^{2-} + SO_4^{2-}$ (B): SO_2 (C): $BaSO_4$

e. $2CH_3COONH_4 + PbSO_4 \rightarrow$
 White ppt.



8.9 IDENTIFICATION OF BASIC RADICALS (CATIONS)

The identification of basic radicals is carried out by performing the following types of tests:

1. Preliminary dry tests

2. Systematic examination in solution i.e., wet tests.

8.9.1 PRELIMINARY DRY TEST

These tests can give very useful information about the cations and anions present in a mixture. Since these tests are neither systematic nor much reliable, not much time should be spent on performing these tests.

8.9.2 COLOUR

Observe colour of the given mixture and draw the conclusion from Table 8.2.

Table 8.2 Colour of the mixture

Colour	Inference	Colour	Inference
Blue	Cupric salts	Yellow or brown	Ferric salts
Green or blue	Hydrated copper salts	Pale pink	Manganese salts
Deep-blue	Anhydrous cobalt salts	Rose-red	Cobalt salts, HgI_2
Green	Hydrated nickel salts	Dark-green or purple	Chromic salts
Light green	Ferrous salts	Colourless	Salts of K , NH_4^+ , Pb , Cd , As , Al , Na , Ca , Ba , Sr

Note: If the salt is colourless; Cu, Fe, Cr, Co, Ni, Mn salts are probably absent.
 Anhydrous copper sulphate is a white solid.
 In a mixture of salts, the dark colour may mask a light colour or the colour may be altogether different.
 In a mixture of coloured salt with a white salt, the absence or presence of the latter cannot be predicted.

9.3 SMELL OF THE SALT OR MIXTURE

Place a pinch of the salt on a watch glass. Moisten it with water and then rub it with your thumb and finger, smell and draw the inference.

Table 8.3 Smell of the mixture

S.No.	Observation	Inference
1.	Smell of NH_3 gas	Ammonium radical, NH_4^+
2.	Smell of rotten eggs	Sulphide (S^{2-})

Note: The absence of any smell does not mean the absence of the radical.

9.4 DENSITY

Put the mixture on a piece of paper and then place it on your palm. Feel its weight as light or heavy.

Table 8.4 Density of the mixture

S.No.	Smell	Inference
1.	Heavy	Pb or Ba salts
2.	Light or fluffy powder	Carbonates of Zn, Mg, Al
3.	Neither light nor heavy	Pb, Ba, Al, Mg and Ca salts may be absent

9.5 DRY-HEATING TEST

Take about 0.5 g of the salt in a clean and dry test tube. Heat it strongly by keeping it almost horizontal over the flame. Observe the changes and infer from the Table 8.5.

Table 8.5 Dry-heating test

S.No.	Observations	Inference
1.	The solid melts	Hydrated salts
2.	The solid swells	Borate, phosphate or alums
3.	Crackling sound on heating	$\text{Pb}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, KBr
4.	A sublimate forms	
i.	White	NH_4^+ , As salts
ii.	Grey or black	Hg salt
iii.	Purple or black solid	Iodide
5.	Change in colour of the salts	
i.	Yellow when hot and white when cold	Zn salt

ii.	Blue when hot and rosy red when cold	Hydrated Co salt
iii.	White when hot and blue when cold	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
iv.	Dark-brown when hot and yellow when cold	Pb salt
v.	Dirty white or yellow when hot and green when cold	Ni, Fe (II) salts
vi.	Black residue	The metal whose oxide is black, Cu, Fe, Co, Ni
vii.	Salt glows on heating	Ca, Mg, Al salts
6.	Evolution of a coloured gas	
i.	Brown gas	Nitrates of heavy metals or bromides
ii.	Violet vapour	Iodides
7.	Water drops in the upper portion of test tubes.	Hydrated salts

8.9.6 FLAME TEST

Certain volatile substances (especially metal chlorides) when heated in a bunsen flame impart a characteristic colour to the flame by means of which the substance can be identified. Colour of the flame is different when it is viewed through a blue or double blue glass.

Procedure:

- Put some conc. HCl in a china dish. Immerse the loop of the platinum wire in conc. HCl and heat it on the non-luminous flame. If it imparts any colour to the flame, repeat the process of immersing it in conc. HCl and then heating it in a flame until the colour is no longer visible.
- Wash the watch glass or china dish and now place a little of the mixture and then moisten it with conc. HCl so that the metal chloride may be produced.
- Take a little of the moistened mass on the loop of a platinum wire and heat it in a bunsen flame.
- Observe the colour of the flame.
 - With naked eye
 - Through a blue glass

Table 8.6 Flame test for cations

Flame colour with naked eye	Flame colour through blue glass	Inference
Dark-green	Bluish-green	Cu^{2+}
Pink-violet	Pink	K^+
Brick-red	Light-green	Ca^{2+}
Grassy-green	Bluish-green	Ba^{2+}
Crimson (deep-red)	Purple	Sr^{2+}

8.9.7 BORAX BEAD TEST

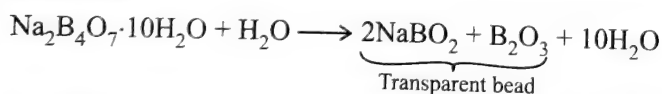
1. Heat the loop of the platinum wire in a flame of the bunsen burner. Then dip the hot loop into powdered borax and again heat it to form a clear, transparent and glassy bead. If the bead obtained is not clear and transparent jerk it off and perform again.
2. Just touch the hot bead with the mixture so that only a few particles stick to it.
3. Then heat it in the oxidising flame and observe colour of the bead when hot. Cool it and again observe its colour when cold.
4. Heat it again but now in the reducing flame and observe its colour when hot. Cool it and again observe its colour when cold.

Table 8.7 Borax bead test

Colour of the bead in oxidising flame		Colour of the bead in reducing flame		Inference	
When hot		When cold	When hot	When cold	
1. Brown		Yellow	Bottle green	Yellow green	Fe
2. Green		Blue	Colourless	Red	Cu
3. Brown		Brown	Grey or black	Grey or black	Ni
4. Pale-purple		Pale-purple	Colourless	Colourless	Mn
5. Green		Green	Green	Green	Cr
6. Blue		Blue	Blue	Blue	Co

8.9.7.1 Chemistry of Borax Bead Test

When powdered borax is heated strongly in a bunsen flame, it loses its water of crystallisation and forms colourless transparent glass like bead which is made up of sodium metaborate and boric anhydride.



Boric anhydride reacts with certain metal salts to form coloured metaborates.

8.9.7.2 In Oxidising Flame

1. $\text{B}_2\text{O}_3 + \text{CuSO}_4 \longrightarrow \text{Cu}(\text{BO}_2)_2 + \text{SO}_3$
 Boric anhydride Copper sulphate Copper metaborate
2. $\text{B}_2\text{O}_3 + \text{NiSO}_4 \longrightarrow \text{Ni}(\text{BO}_2)_2 + \text{SO}_3$
 Nickel sulphate Nickel metaborate
3. $\text{B}_2\text{O}_3 + \text{CoSO}_4 \longrightarrow \text{Co}(\text{BO}_2)_2 + \text{SO}_3$
 Cobalt sulphate Cobalt metaborate
4. $\text{B}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \longrightarrow 2\text{Fe}(\text{BO}_2)_3$
 Ferric oxide Ferric metaborate

8.9.7.3 In Reducing Flame

Certain metaborates are reduced to the free metal in a reducing flame. For metals with variable valence, the metaborate changes to lower valence state.

1. $2\text{Cu}(\text{BO}_2)_2 + \text{C} \longrightarrow 2\text{CuBO}_2 + \text{B}_2\text{O}_3 + \text{CO}$
 $2\text{CuBO}_2 + \text{C} \longrightarrow 2\text{Cu} + \text{B}_2\text{O}_3 + \text{CO}$
2. $\text{Ni}(\text{BO}_2)_2 + \text{C} \longrightarrow \text{Ni} + \text{B}_2\text{O}_3 + \text{CO}$
3. $2\text{Fe}(\text{BO}_2)_3 + \text{C} \longrightarrow 2\text{Fe}(\text{BO}_2)_2 + \text{B}_2\text{O}_3 + \text{CO}$

8.9.7.4 Notes for Borax Bead Test

1. Only coloured salts give borax bead test. Do not perform this test if the salt is colourless.
2. The bead should be clear, transparent and glass like. If it is not so, jerk it off from the loop and start afresh.
3. While heating, the loop of the platinum wire should be kept vertical.
4. Only a few particles of the mixture should be taken for the borax bead test.
5. Observe the colour of bead, when hot as well as when cold.

8.9.8 CHARCOAL CAVITY TEST

Procedure:

1. Bore a fresh cavity in a clean charcoal block with the help of a knife or cavity borer.
2. Mix about (5–10 mg) of powdered salt with about (40–50 mg) of anhydrous sodium carbonate or **fusion mixture (mixture of equal amounts of Na_2CO_3 and K_2CO_3)**.
3. Place small amount of the salt into a freshly bored cavity, press it with 1–2 drops of water.
4. Put this mixture to flame by means of a blow pipe for 2–5 min.
5. Observe the colour of bead, the colour of residue and the colour of incrustation formed if any when hot as well as when cold.

Table 8.8 Charcoal cavity test

Colour of residue or incrustation		Colour of bead		Inference
When hot		When cold		
1. Yellow		White	None	Zn
2. Dark-red brown		Yellow	Soft white marks paper	Pb
3. Chocolate brown		Chocolate brown	None	Cd
4. Red flakes		Red flakes	Red flakes	Cu
5. White		White (garlic odour)	None	As

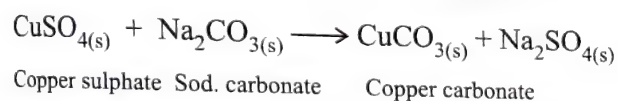
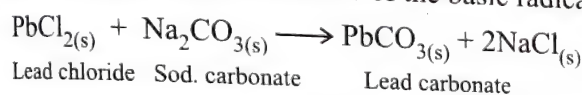
6.	None	None	Slightly white does not mark paper	Ag
7.	Black	Black	None	Fe, Co, Ni, Mn
8.	White	White	None	Ca, Ba, Sr, Al, Mg

Note:

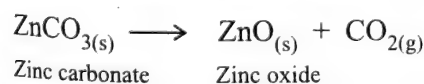
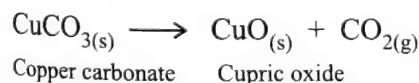
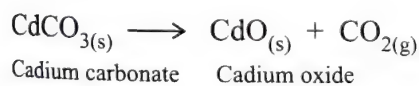
1. Perform the test with a newly-bored cavity.
2. The cavity should not be deep.
3. The mixture should be moistened with a drop of water. Otherwise, there are every chances of it being blown away.
4. The mixture should be completely covered with flame while heating.
5. Any deflagration of the mixture on heating indicates the presence of nitrate.

8.9.8.1 Chemistry of Charcoal Cavity Test

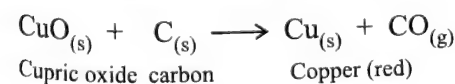
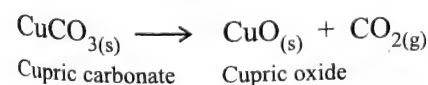
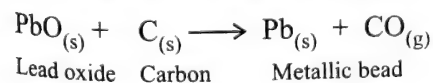
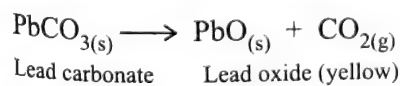
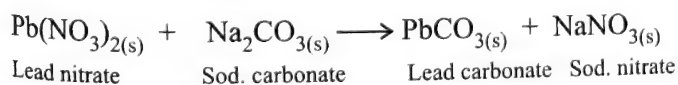
Heating of the given salt with solid sodium carbonate or fusion salt forms the corresponding carbonates of the basic radicals.



1. Metal carbonates decompose into metal oxides. The metal oxides, if volatile, form incrustation (crust) around the cavity.



2. The unstable metallic oxides further decompose into free metals to form metallic beads or scales.



8.9.9 COBALT NITRATE TEST OR RINMANN'S TEST

Procedure:

1. Bore a fresh cavity in a charcoal block.
2. Place the given salt alone in this cavity and heat it for 10–15 sec with flame using blow-pipe.
3. Cool it, add 1–2 drops of cobalt nitrate solution and then heat it with the tip of the flame (oxidising) using blow pipe.
4. Observe the colour of the residue.

Table 8.9 Cobalt nitrate test

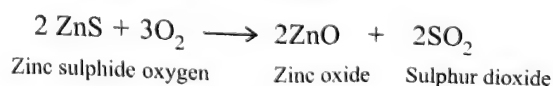
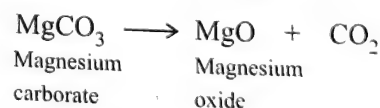
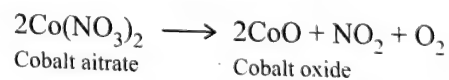
Colour of residue		Inference	Composition of bead
1.	Green residue	Zn	CoO·ZnO
2.	Pink residue	Mg	CoO·MgO
3.	Blue residue	Al when PO_4^{3-} and BO_3^{3-} are absent	CoO·Al ₂ O ₃
4.	Blue residue	PO_4^{3-} in absence of Al	NaCo ₃ PO ₄

Note:

1. Cobalt nitrate test is performed only when residue left in the charcoal cavity test is white.
2. Only zinc, magnesium and aluminium radicals can be detected with this test.
3. Do not add more than two drops of cobalt nitrate, otherwise the residue obtained is black mass.
4. Performing cobalt nitrate test with white residue left in the charcoal cavity test should be avoided. Instead, bore a fresh cavity and use the given mixture alone.

8.9.9.1 Chemistry of Cobalt Nitrate Test

Cobaltous oxide produced by the decomposition of cobalt nitrate combines with the metallic oxide formed to form 'double oxides' which have characteristics colours.



- i. $\text{CoO} + \text{ZnO} \longrightarrow \text{CoZnO}_2$ (Cobalt zincate) or $\text{CoO} \cdot \text{ZnO}$
Cobalt oxide Zinc oxide Green
- ii. $\text{CoO} + \text{Al}_2\text{O}_3 \longrightarrow \text{Co(AlO}_2)_2$ or $\text{CoO} \cdot \text{Al}_2\text{O}_3$
Cobalt oxide Aluminium oxide Blue (Cobalt metaaluminate)



Cobalt oxide Magnesium oxide Dirty-pink

8.9.10 MICROCOSMIC SALT BEAD TEST

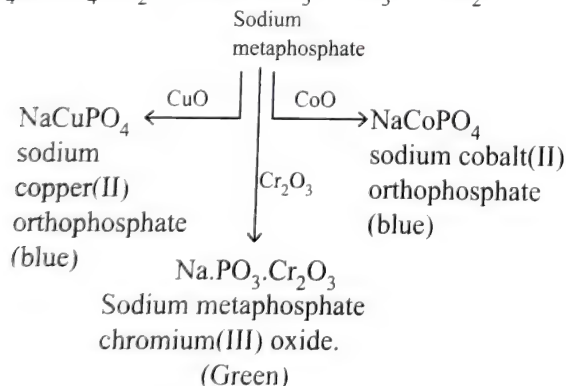
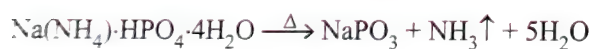
Sodium ammonium hydrogen phosphate tetrahydrate

($\text{Na}(\text{NH}_4)\text{H}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$, called microcosmic salt, gives on fusion a similar glassy, colourless bead as borax does. The salt on fusion is first dehydrated which then forms sodium meta-phosphate (NaPO_3) as colourless bead which reacts with the metallic oxides giving coloured beads due to the formation of coloured orthophosphates. This test is suitable for Cu, Cr and Co, the colours for the corresponding metals being the same as for those of borax beads.

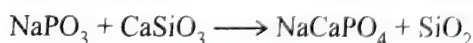
Table 8.10 Microcosmic salt bead test

	Colour	Composition	Cation
1.	Blue bead with CuO	NaCuPO_4 sodium copper(II) orthophosphate	Cu^{2+}
2.	Brown bead with CoO	NaCoPO_4 Sodium cobalt (II) orthophosphate	Co^{2+}
3.	Green bead with Cr_2O_3	$\text{NaPO}_3 \cdot \text{Cr}_2\text{O}_3$	Cr^{+3}

8.9.10.1 Chemical Reactions Involved



Many silicates form a white translucent bead because they react with NaPO_3 and set free SiO_2 , which remains undissolved in the bead. Thus this test is useful for the detection of silicates also.



8.10 APPLICATIONS OF K_{sp} IN QUALITATIVE SALT ANALYSIS

The separation and identification of various basic radicals into different group is mainly based upon six groups based on the increasing K_{sp} values of corresponding precipitating compounds.

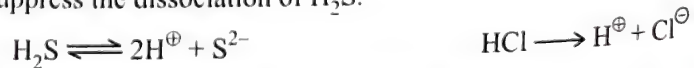
Group	Group reagent	Cations	Cations precipitated as
I.	Dilute HCl (2M) in cold	Hg_2^{2+} , Ag^+ , Pb^{2+}	Hg_2Cl_2 , AgCl , PbCl_2 (PbCl_2 is soluble in hot water, less in cold water)
II.	H_2S in presence of 0.2M HCl	II A: Hg^{2+} , Pb^{2+} , Bi^{3+} , Cu^{2+} , Cd^{2+} II B: As^{3+} , As^{5+} , $\text{Sb}^{3+/+5}$, $\text{Sn}^{2+/4+}$	HgS , PbS , Bi_2S_3 , CuS , CdS As_2S_3 , As_2S_5 , Sb_2S_3 , Sb_2S_5 , SnS , SnS_2
III.	NH_4Cl + NH_4OH	Fe^{3+} , Cr^{3+} , Al^{3+}	$\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$
IV.	H_2S in basic medium, i.e. H_2S + NH_4OH	Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+}	CoS , NiS , MnS , ZnS
V.	NH_4Cl + NH_4OH + $(\text{NH}_4)_2\text{CO}_3$	Ba^{2+} , Sr^{2+} , Ca^{2+}	BaCO_3 , SrCO_3 , CaCO_3
VI.	No specific reagent	Na^+ , K^+ , Mg^{2+}	—
Zero	Nessler's reagent in ammonical solution $\text{K}_2[\text{HgI}_4]$ + NH_4OH	NH_4^+	Iodide of Millon's base (Oxydimercuric ammonium iodide) $\text{O} \begin{array}{c} \text{Hg} \\ \text{Hg} \end{array} \text{NH}_2\text{I}$

Increasing K_{sp} values ↓

Group I: Dilute HCl is added to the solution containing cations. Since the K_{sp} values of the chlorides of group I is less than K_{sp} values of the chlorides of higher group, so only the chlorides of group I are precipitated.

If the concentrated HCl is used, then $[\text{Cl}^-]$ will increase, then the ionic product (Q_{sp}) of their chlorides will increase, so chlorides of other group may be precipitated. Moreover, PbCl_2 is soluble in conc. HCl.

Group II: $\text{H}_2\text{S}_{(g)}$ is passed in an acidic medium to the solution containing cations. Since the K_{sp} values of the sulphides of group II ($\approx 10^{-28}$ – 10^{-54}) is less than K_{sp} values of the sulphides of higher gp. ($>10^{-28}$), so only the sulphides of group II are precipitated. H_2S is a weak acid and its dissociation can be suppressed to get low $[\text{S}^{2-}]$ such that ionic products of group II sulphides are exceeded but not those of group III sulphides. This condition is achieved by passing H_2S in an acid medium so that H^+ (the common ion) suppress the dissociation of H_2S .

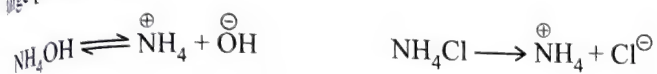


Thus, the group II sulphides are precipitated but not of other groups under these conditions because their K_{sp} values are quite high.

Note: Pb^{2+} is included in both groups I and II. $PbCl_2$ is sparingly soluble in dil. HCl. Any Pb^{2+} ion present in group I filtrate will get precipitated as PbS in group II.

Group III: Hydroxides of group III are precipitated by adding an excess of solid NH_4Cl to the solutions of these cations followed by the addition of excess of NH_4OH .

NH_4OH is a weak base and is slightly ionised, whereas NH_4Cl being a strong electrolyte, ionises almost completely to give large $[NH_4^+]$ ions.



Due to common ion effect, the suppression of ionisation of NH_4OH occurs and $[OH^-]$ decreases appreciably. But even with this low $[OH^-]$ ions, exceed the low value of the K_{sp} of their hydroxides. Hence, only the hydroxides of group III get precipitated but not of other groups under these conditions because the K_{sp} of their hydroxides are quite high.

Note:

1. $NaOH$ cannot be used in place of NH_4OH being a strong base, $[OH^-]$ will be high, and hence the hydroxides of the other group will precipitate out.
2. NH_4OH should be added only after adding NH_4Cl otherwise common ion effect would not occur in absence of NH_4Cl . Hence, hydroxides of other group will be precipitated out.
3. $NaCl$ and $NaOH$ cannot be used in place of NH_4Cl and NH_4OH . Both being strong ionises completely to give high $[OH^-]$. $NaCl$ cannot suppress the ionisation of $NaOH$. Therefore, hydroxides of other group will precipitate out. Moreover, $Al(OH)_3$ and $Cr(OH)_3$ are soluble in excess of $NaOH$ because of the formation of aluminate and chromate, respectively.

Group IV: Precipitation of sulphides of group IV occurs in presence of large excess of NH_4OH . K_{sp} of sulphides of group IV are sufficiently high. Therefore high concentration of S^{2-} ions as compared to that required in group II is needed for which K_{sp} values are low).

H_2S is weakly ionised as:

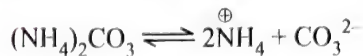


In presence of NH_4OH , OH^- ions neutralise H^+ ions. According to Le Chatelier's principle, ionisation of H_2S proceeds in forward direction. Therefore, $[S^{2-}]$ increases. Ultimately, the ionic products of the sulphides of group IV exceeds the K_{sp} values of their corresponding metal sulphides and hence get precipitated.

Note: $(NH_4)_2SO_4$ cannot be used in place of NH_4OH , because the sulphates of Ba, Ca and Sr will get precipitated as white precipitate.

Group V: The carbonates of group V are precipitated by adding $(NH_4)_2CO_3$ solution to the solution of these cations in the presence

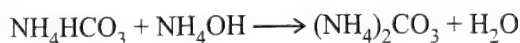
of NH_4Cl and NH_4OH . $(NH_4)_2CO_3$ is a weak electrolyte that ionises slightly to give small $[CO_3^{2-}]$ ions.



NH_4Cl is a strong electrolyte, ionises almost completely to give large $[NH_4^+]$. Due to the common ion effect, the dissociation of $(NH_4)_2CO_3$ is suppressed and hence high $[CO_3^{2-}]$ decreases considerably. But even with this low $[CO_3^{2-}]$ ions, the ionic products of these cations and CO_3^{2-} ions exceed the low K_{sp} values of their corresponding metal carbonates and thus get precipitated.

Note: However, under these conditions, Mg salts do not get precipitated as $MgCO_3$ since its K_{sp} value is comparatively high and thus requires a high $[CO_3^{2-}]$ ions for precipitation. The carbonates of Na^+ , K^+ and NH_4^+ are also not precipitated because they are quite soluble.

The necessity of adding NH_4OH arises due to the fact that $(NH_4)_2CO_3$ solution usually contains a large amount of NH_4HCO_3 . Thus, the cations of group V will form not only insoluble carbonates but also soluble bicarbonates. As a result, the precipitation will not be complete. In order to convert NH_4HCO_3 , NH_4OH is always added.



Note:

1. Na_2CO_3 cannot be used in place of $(NH_4)_2CO_3$ because Na_2CO_3 is a strong electrolyte whose ionisation cannot be suppressed by common ion effect. Therefore, the large $[CO_3^{2-}]$ ions will also precipitate magnesium.
2. Large excess of NH_4Cl should be avoided. Since the large excess of NH_4Cl further reduces the $[CO_3^{2-}]$ ions, to such a low value that it even does not exceed the K_{sp} values of group V radicals.
3. The solution should be warmed and not boiled while precipitating group V radicals. Since warming decomposes the soluble bicarbonates (impurities) of Ca, Sr and Ba into insoluble carbonates.



Boiling dissolves the insoluble carbonates as chlorides.



4. The group V precipitates should be dissolved in acetic acid. If the precipitates are dissolved in strong acid like HCl or HNO_3 , Ca will not get precipitated as calcium oxalate by adding ammonium oxalate because it is soluble in strong acid.

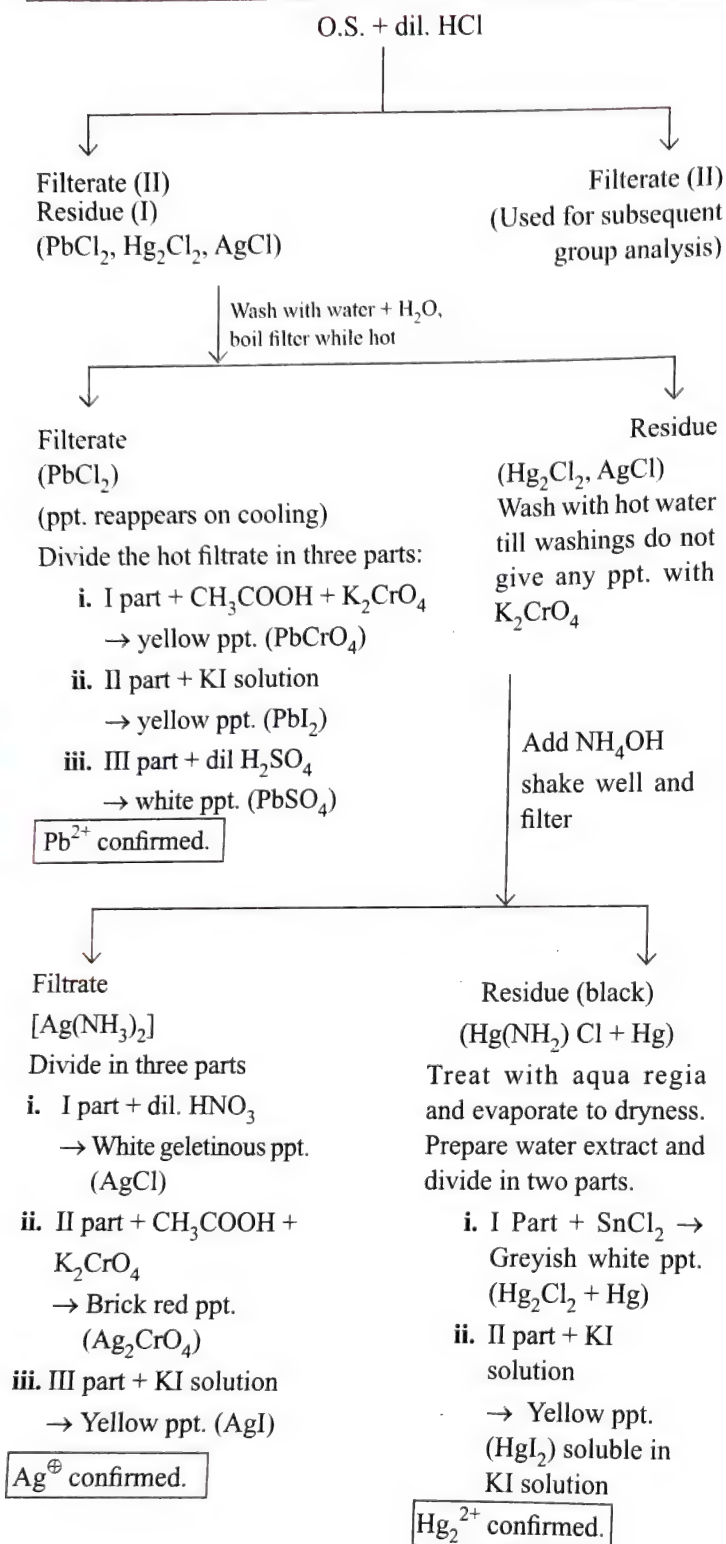
H_2SO_4 precipitates sulphates of Ca, Ba and Sr.

8.11 ANALYSIS OF GROUP I

$(Ag^+, Pb^{2+}, Hg_2^{2+})$

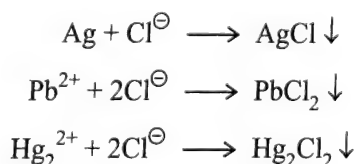
Group reagent is dil. HCl. Chlorides of Pb^{2+} , Hg_2^{2+} , Ag^+ are precipitated on addition of dil. HCl to solution of mixture (original solution)

(O.S.) + Filter.

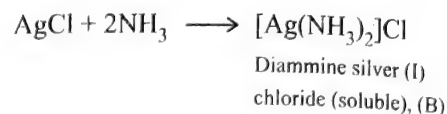


8.11.1 CHEMICAL REACTIONS INVOLVED

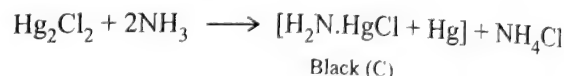
Ag⁺, Pb²⁺, Hg₂²⁺ are precipitated as insoluble chlorides on adding dil. HCl to aqueous solution. If no ppt. appears than group I is absent.



- Filter the ppt. Filtrate is used for identification of group II.
- PbCl₂(A) is soluble in hot water and thus separated.
- AgCl is soluble in aqueous NH₃ as [Ag(NH₃)₂]Cl



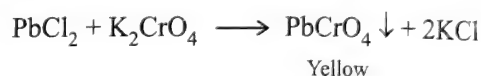
- Hg₂Cl₂ is blackened by NH₃



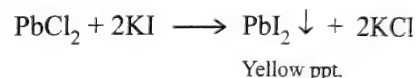
Pb²⁺:

A: Soluble PbCl₂ (in hot water) solution.

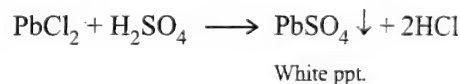
- (A) + K₂CrO₄ → Yellow ppt.



- (A) + KI → Yellow ppt.



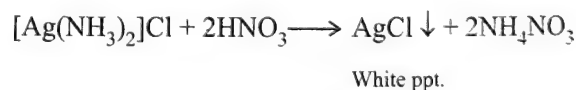
- (A) + H₂SO₄ → White ppt.



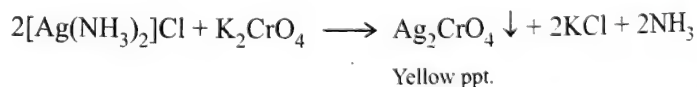
Ag⁺:

B: Soluble [Ag(NH₃)₂]Cl

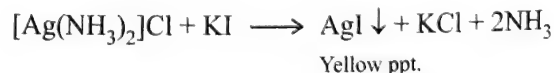
- (B) + HNO₃ → White ppt.



- (B) + K₂CrO₄ → brick red ppt.



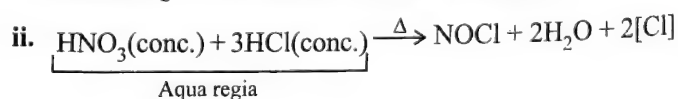
- (B) + KI → yellow ppt.

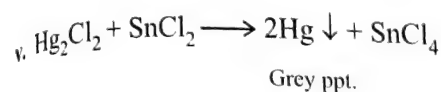
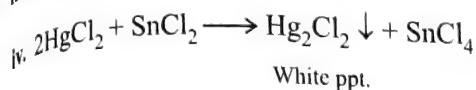
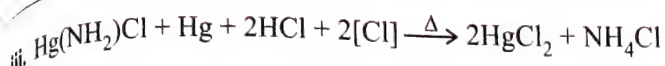


Hg₂²⁺:

Black [Hg(NH₂)Cl + Hg] + aqua regia and heat to dissolve the black ppt.

- Add SnCl₂ → White ppt. changing to grey.





vi. Add KI solution \longrightarrow yellow ppt. soluble in KI solution.

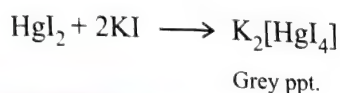
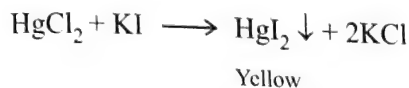


ILLUSTRATION 8.5

Colourless salt (A) $\xrightarrow{\text{dil. HCl}}$ White ppt. (B)
Soluble in H_2O Soluble in hot water

\downarrow (i) FeSO_4
 \downarrow (ii) conc. H_2SO_4

Brown colour ring (D) Yellow ppt. (C)

Identify (A), (B), (C) and (D).

Sol. (A): $\text{Pb}(\text{NO}_3)_2$ (B): PbCl_2
(C): PbI_2 (D): $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$

ILLUSTRATION 8.6

Identify (A), (B), (C) and (D) in the following:
Colourless salt (A) + conc. $\text{H}_2\text{SO}_4 \longrightarrow$ Brown fumes intensified on adding Cu turnings.
Aqueous solution (A) + Cu \longrightarrow Blue coloured solution (B) and metal (C).
Aqueous solution (A) + HCl \longrightarrow White ppt. soluble in aqueous NH_3 forming (D).

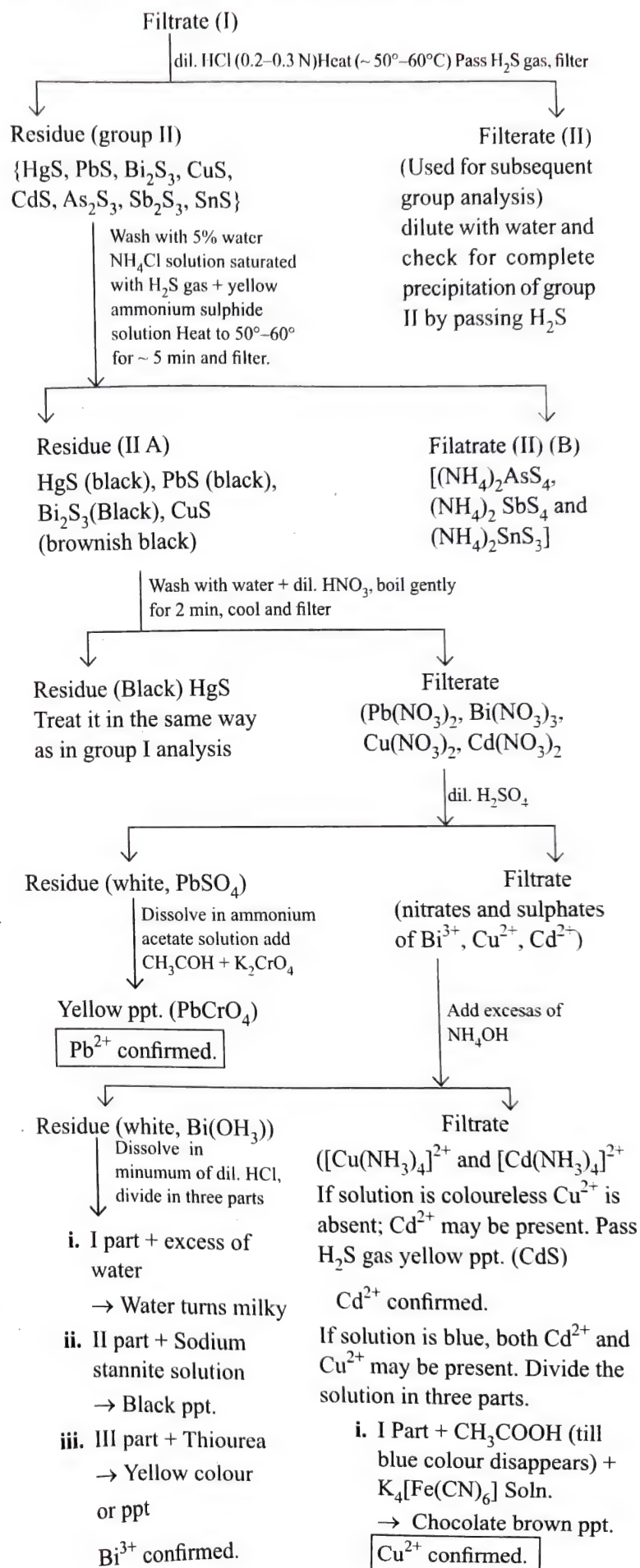
Sol. (A): AgNO_3 (B): $\text{Cu}(\text{NO}_3)_2$
(C): Ag (D): $[\text{Ag}(\text{NH}_3)_2\text{Cl}]$

ILLUSTRATION 8.7

Salt (A) makes part of electrode and is soluble in water. (A) is blackened by NH_3 forming (B). (B) is soluble in aqua regia forming (C). (C) gives orange ppt. with KI but ppt. dissolves in excess of KI forming (D). Identify (A), (B), (C) and (D).

Sol. (A): Hg_2Cl_2 (calomel)
(B): $(\text{HgNH}_2\text{Cl} + \text{Hg})$
(C): HgCl_2
(D): $\text{K}_2[\text{HgI}_4]$

8.12 ANALYSIS OF GROUP II



- ii. II part + conc. HCl + Pass $\text{H}_2\text{S}_{(\text{g})}$
 → Black ppt. of CuS , filter and dilute the filtrate and pass H_2S gas again → Yellow ppt. (CdS)

Both Cu^{2+} and Cd^{2+} confirmed.

- iii. III part + KCN soln. (till blue colour disappears) + H_2S → yellow ppt of CdS

Cd^{2+} confirmed.

Filtrate (II B)

(i) dil HCl, (ii) conc. HCl and boil for 5 min dilute with water (2–3 mL) and filter

Residue
(yellow, As_2S_3)

Dissolve in conc. HNO_3
Divide in two parts

- i. I part + excess of ammonium molybdate solution boil and cool → Canary yellow ppt.

As^{3+} confirmed.

- ii. II part + Boil to dryness.

Extract with NH_4OH .

Add $\text{Mg}(\text{NO}_3)_2$ solution, stir and allow to stand → White crystalline ppt [$\text{Mg}(\text{NH}_4)\text{AsO}_4$] In the ppt. and $\text{CH}_3\text{COOH} + \text{AgNO}_3$ Red-brown ppt. of Ag_3AsO_4

As^{3+} confirmed.

Filtrate
(SbCl_3 , SnCl_4)

Boil off H_2S gas
Divide in three parts

- i. I Part + Al wire (2–3 pieces) and warm gently for 5 min. Filter.

Residue,
Black, Sb^{3+}

Filtrate
Add HgCl_2 solution → greyish white ppt.

Sn^{2+} confirmed.

- ii. II part + NH_4OH (in excess) oxalic acid (solid). Warm and pass H_2S gas. Filter.

Residue,
orange,
 Sb_2S_3

Filtrate
Boil off H_2S . Add few drops of FeCl_3 + DMG solution + tartaric acid + NH_4OH (till basic) Red colouration.

Sn^{2+} confirmed.

- iii. III part + add excess of water → water becomes milky

Sb^{3+} confirmed.

8.12.1 CHEMICAL REACTIONS INVOLVED

Group II: Hg^{2+} (mercuric).

II A: Pb^{2+} , Bi^{3+} , Cu^{2+} , Cd^{2+} II B: As^{3+} , Sb^{3+} , Sn^{2+} , Sn^{4+}

Group reagent: $\text{H}_2\text{S}_{(\text{g})}$ in presence of HCl

These radicals are precipitated as their sulphides while the sulphides of other metals remain in solution because of their high solubility product. HCl acts as a source of H^+ and thus decreases the concentration of S^{2-} (common-ion-effect). Hence, the decreased concentration of S^{2-} is sufficient to precipitate the group II metals due to their low K_{sp} values. (Group IV metals have high solubility products)

PbS , HgS , Bi_2S_3 , CuS (black);

CdS , SnS_2 , As_2S_3 (yellow)

Sb_2S_3 (orange);

SnS (brown)

1. PbS , CdS are precipitated in dilution only due to higher K_{sp} .

$\text{PbCl}_2 \xrightarrow{\text{Hot water}} \text{Dissolved} \xrightarrow{\text{Cooling}} \text{ppt of } \text{PbCl}_2 \text{ reappears}$
White

$\text{Pb}^{2+} + \text{CrO}_4^{2-} \longrightarrow \text{PbCrO}_4$
Yellow

$\text{Pb}^{2+} + \text{SO}_4^{2-} \longrightarrow \text{PbSO}_4$
White

$\text{Pb}^{2+} + \text{OH}^- \longrightarrow \text{Pb}(\text{OH})_2$
White

$\downarrow \text{NaOH (excess)}$

$\text{Na}_2\text{PbO}_2 \xrightarrow{\text{Oxidised}} \text{Na}_2\text{PbO}_3$

$\text{PbS} + 3/2\text{O}_2 \xrightarrow{300^\circ\text{C}} \text{PbO} + \text{SO}_2$
Yellow (Massicot)

$\text{PbO} \xrightarrow{900^\circ\text{C}} \text{PbO}$

Yellow (Massicot) Red (litharge)

2. IIA sulphides are insoluble in yellow ammonium sulphides and IIB sulphides are soluble in it.
 3. HgS is insoluble in dilute HNO_3 while PbS , Bi_2S_3 , CuS , CdS are soluble in it.
 4. In water, Bi_2S_3 , CuS , CdS etc are soluble to give respective hydroxides, but PbSO_4 is not soluble.
 5. Hydroxides formed above in (4):

$\text{Bi}(\text{OH})_3$ is insoluble in NH_4OH .

$\text{Cu}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$ form soluble complexes.

$\text{Bi}(\text{SO}_4)_3 + 6\text{NH}_4\text{OH} \longrightarrow 2\text{Bi}(\text{OH})_3 \downarrow + 3(\text{NH}_4)_2\text{SO}_4$

$\text{CuSO}_4 + 4\text{NH}_4\text{OH} \longrightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4 + 4\text{H}_2\text{O}$
(Deep blue)

$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 + 4\text{CH}_3\text{COOH} \longrightarrow$

$\text{CuSO}_4 + 4\text{CH}_3\text{COONH}_4$

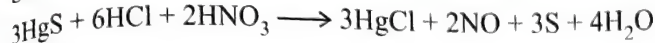
$\text{CuSO}_4 + \text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] \downarrow + 2\text{K}_2\text{SO}_4$
Red brown ppt.

$\text{CdSO}_4 + 4\text{NH}_4\text{OH} \longrightarrow [\text{Cd}(\text{NH}_3)_4]\text{SO}_4 + 4\text{H}_2\text{O}$
(Colourless)

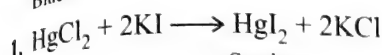
$[\text{Cd}(\text{NH}_3)_4]\text{SO}_4 + \text{H}_2\text{S} \longrightarrow \text{CdS} \downarrow + (\text{NH}_4)_2\text{SO}_4 + 2\text{NH}_3$
Yellow

Note: HgS is only sulphide of group II which does not dissolve in conc. HNO₃

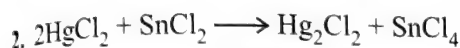
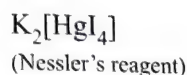
So, aqua regia (HCl + HNO₃) (3 : 1) is used to dissolve it.



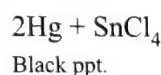
Black



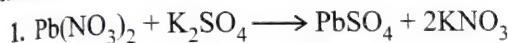
Scarlet
red ppt.



White ppt.

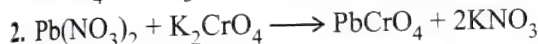
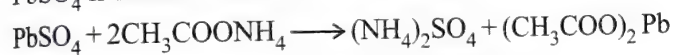


Tests for Pb²⁺:

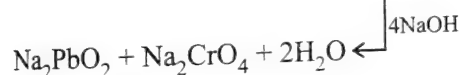


White

PbSO₄ is soluble in ammonium acetate

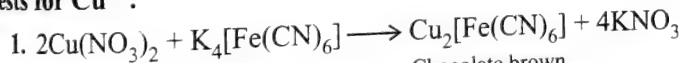


Yellow ppt

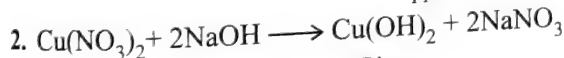


Yellow soln.

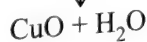
Tests for Cu²⁺:



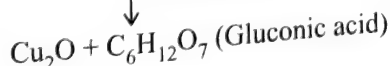
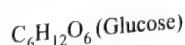
Chocolate brown
ppt.



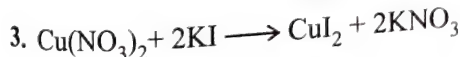
Blue



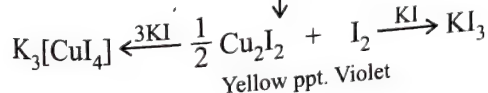
Black



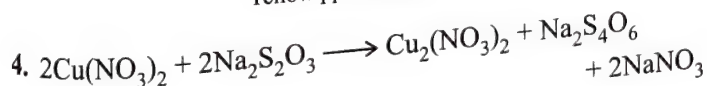
Red



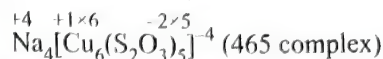
Brown



Yellow ppt. Violet

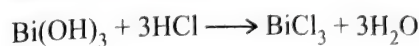


White

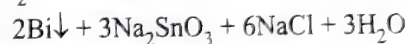
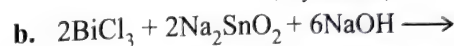


For remembrance	4	6	5	465 complex
	Na	Cu	S ₂ O ₃	

5. Bi(OH)₃ is soluble in dilute HCl to form BiCl₃ which is tested in two ways.



White ppt
(oxychloride)

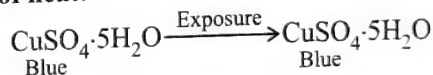


Black

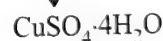
6. Arsenic sulphides is insoluble in conc. HCl while Sb, Sn sulphides are soluble. Sb₂S₃ can be precipitated in presence of oxalic acid.

7. Cu and Cd separation is based on fact that in presence of KCN, only Cd is precipitated as sulphides on passing H₂S.

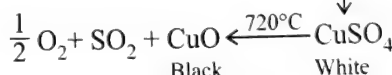
Effect of heat:



Blue

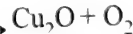


Bluish white



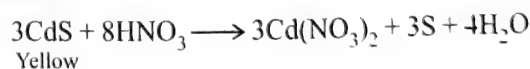
Black

White

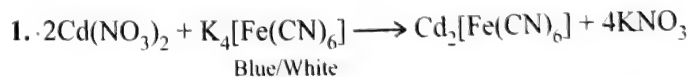


Red

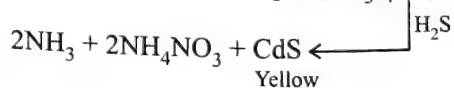
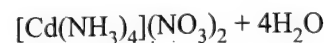
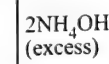
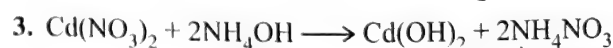
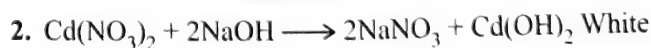
Tests for Cd²⁺:



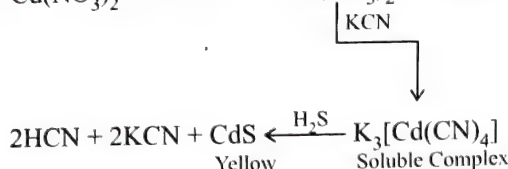
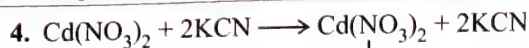
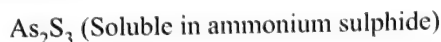
Yellow



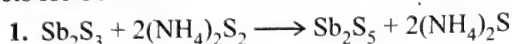
Blue/White



Yellow

**Tests for As^{3+} :**

Yellow

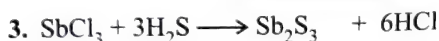
Tests for Sb^{3+} :

Orange

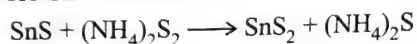
Orange



White turbidity

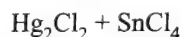
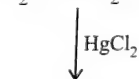
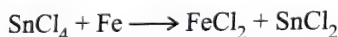
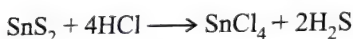
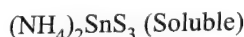
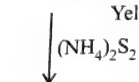


Orange

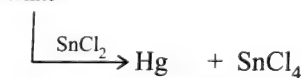
Tests for Sn^{2+} and Sn^{4+} :

Brown

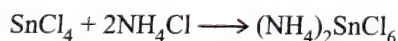
Yellow



White



Grey/Black



Pink

Note: $(\text{NH}_4)_2\text{SnCl}_6$ or pink salt is used as mordant which holds the dyes in clothes.

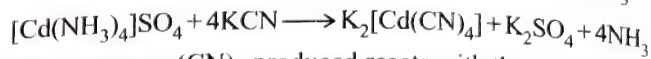
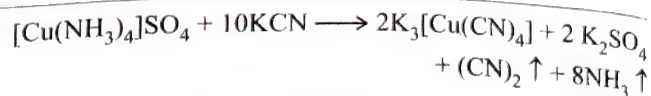
Analysis of both Cu^{2+} and Cd^{2+} present in the given mixture:

- By fractional precipitation of Cu and Cd (using H_2S gas):
- Solution $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ and $[\text{Cd}(\text{NH}_3)_4]\text{SO}_4$ + conc. HCl
 $\xrightarrow{\text{Pass H}_2\text{S gas}}$ black ppt. (CuS).

Filter. Dilute the filtrate using water and pass H_2S gas \longrightarrow yellow ppt. (CdS).

This test is based on the difference in solubility product of CuS (8.5×10^{-45}) and CdS (3.6×10^{-29}). When $\text{H}_2\text{S}(\text{g})$ is passed in presence of conc. HCl, only copper precipitates out. On dilution, the concentration of HCl decreases, enabling precipitation of CdS .

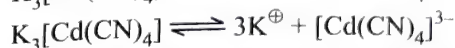
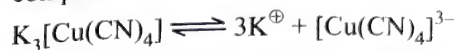
- KCN test:** When filtrate is blue, addition of excess of KCN forms soluble colourless complexes with Cu and Cd respectively.



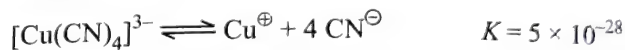
The cyanogen $(\text{CN})_2$ produced reacts with the solution.



In cyanide complex copper is more stable than cyanide complex of cadmium. The primary ionisation of both complexes is as under:



The secondary ionisation and ionisation constant of these complexes are:



With $\text{K}_3[\text{Cu}(\text{CN})_4]$, the concentration of Cu^+ ions produced by the secondary ionisation of the complex into $[\text{Cu}(\text{CN})_4]^{3-}$ is insufficient to exceed the solubility product of Cu_2S on passing H_2S , hence no precipitation occurs. Whereas, secondary ionisation of $\text{K}_3[\text{Cd}(\text{CN})_4]$, is comparatively high, therefore enough Cd^+ ions are available in the soluble and when H_2S gas is passed, yellow ppt. of CdS is obtained.

In this way Cd^{2+} can be identified in presence of Cu^{2+} ions.

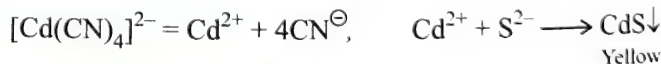
ILLUSTRATION 8.8

If Cu^{2+} and Cd^{2+} both are present, it is difficult to analyse. Outline a scheme to analyse in a mixture.

Sol. KCN forms complex with Cu^{2+} and Cd^{2+}



When H_2S gas is passed, unstable complex of Cd^{2+} gives yellow ppt.

**ILLUSTRATION 8.9**

HgS is soluble in aqua regia forming HgCl_2 . What happens if Cu turnings are added to HgCl_2 ?

Sol. $\text{HgCl}_2 + \text{Cu} \longrightarrow \text{CuCl}_2 + \text{Hg}$. Hg is deposited on Cu.

ILLUSTRATION 8.10

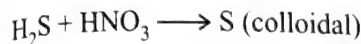
Identify (A), (B), (C), (D) and (E). (A) (black) + dil. HCl $\xrightarrow{\Delta}$ (B) (solution) + (C) (gas). Gas (C) turns lead acetate paper black. (B) gives orange ppt. (D) soluble in excess of KI forming (E).

Sol. (A): HgS , (B): HgCl_2 , (C): H_2S , (D): HgI_2 , (E): K_2HgI_4

ILLUSTRATION 8.11

Sometimes it happens that when H_2S gas is passed into solution in dil. HCl, yellowish white turbidity appears. What do you conclude? What precautions are taken to check this turbidity?

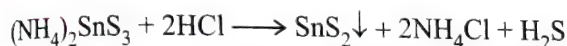
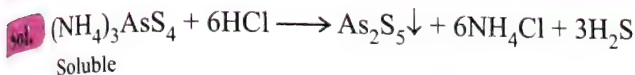
Sol. This yellowish white turbidity is due to colloidal sulphur, formed by oxidation of H_2S by the presence of NO_3^- or NO_2^- or SO_3^{2-} .



Before passing H_2S gas, solution is boiled so as to decompose these radicals.

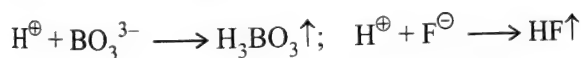
ILLUSTRATION 8.12

IIIb (Arsenic group) sulphides are soluble in YAS. If conc. HCl is added to this soluble portion, coloured ppt. are formed. Write reactions.

**8.13 REMOVAL OF INTERFERING RADICALS**

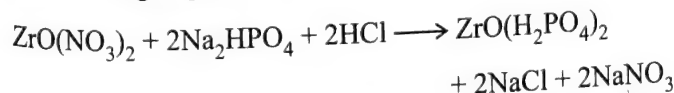
In a china-dish, add centrifugate of group II, boil off H_2S gas (check for the complete removal of H_2S gas by using lead acetate paper) \longrightarrow solution (1).

- a. When BO_3^{3-} or F^- is present: In the above solution (1), add conc. HCl, boil to dryness, repeat this process for 2–3 times. Add water (distilled) and proceed for the analysis of group III radicals

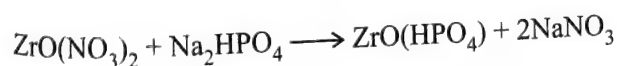
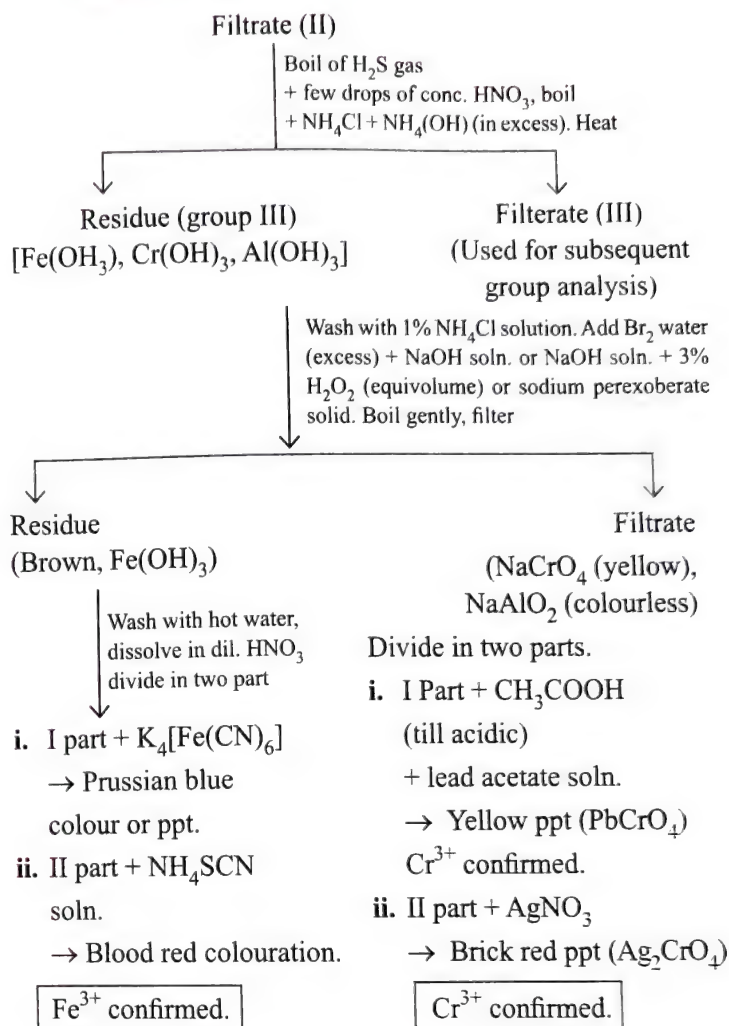


- b. When $\text{C}_2\text{O}_4^{2-}$ is present: In the solution (1), add conc. HNO_3 , boil to dryness repeat this process for 2–3 times. Add distilled water and proceed for the analysis of group III radicals.

- c. When PO_3^{3-} is present: In the solution (1), add dil. HCl (Normality should not exceed 1N), add NH_4Cl solid, till it is dissolved. Add 2–3 drops of zirconyl nitrate reagent or zirconium nitrate reagent. White ppt. obtained is rejected. Repeat this process. Take the centrifugate obtained for the analysis of group III radicals.



or

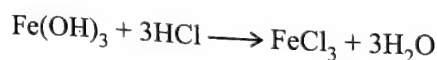
**8.14 ANALYSIS OF GROUP III****8.14.1 CHEMICAL REACTIONS INVOLVED**

Boil off H_2S from the filtrate of group II. Add NH_4Cl and one drop of dil. HNO_3 ; heat, cool and add $\text{NH}_4\text{OH} \longrightarrow$ ppt.

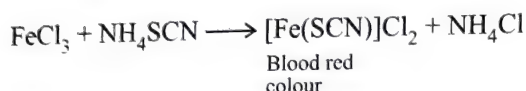
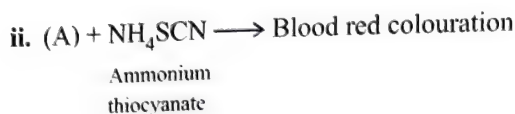
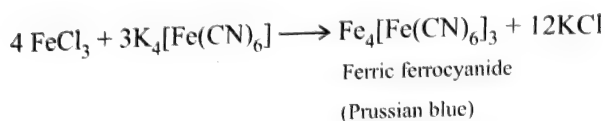
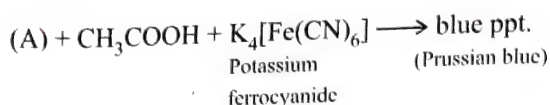
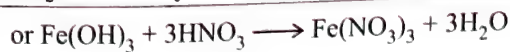
- i. Reddish brown ppt. of $\text{Fe}(\text{OH})_3$ if Fe^{3+} is present (salt is brown).
- ii. Dirty green ppt. of $\text{Cr}(\text{OH})_3$ if Cr^{3+} is present (salt is green).
- iii. White ppt. of $\text{Al}(\text{OH})_3$ if Al^{3+} is present (salt is colourless).
- iv. Dil. HNO_3 is added to oxidise Fe^{2+} (light green) into Fe^{3+} (deep yellow).
- v. NH_4Cl by common ion effect decreases ionisation of NH_4OH .

Fe^{3+} :

- i. $\text{Fe}(\text{OH})_3$ ppt. are insoluble in NaOH but soluble in conc. HCl /dil. HNO_3



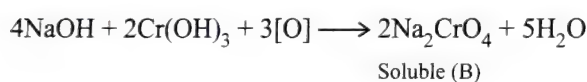
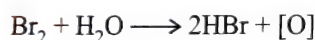
Soluble (A)



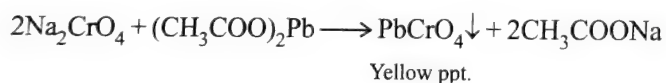
Fe^{2+} does not give these tests, hence at the start of the group, HNO_3 is added to oxidise Fe^{2+} to Fe^{3+} .

Cr^{3+} :

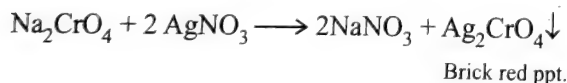
- i. $\text{Cr}(\text{OH})_3$ (green ppt.) are insoluble in NaOH but dissolve in presence of Br_2 water (oxidising agent) giving yellow coloured Na_2CrO_4 solution.



- ii. $(\text{B}) + \text{CH}_3\text{COOH} + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow \text{yellow ppt.}$

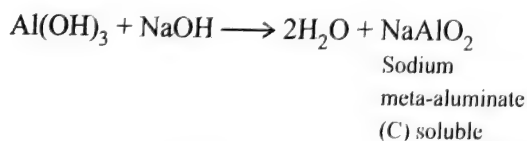


- iii. $(\text{B}) + \text{AgNO}_3 \longrightarrow \text{brick red ppt.}$



Al^{3+} :

- i. White ppt. of $\text{Al}(\text{OH})_3$ (salt is colourless) + NaOH solution (excess) \longrightarrow ppt. dissolves forming NaAlO_2 .



- ii. White ppt. reappears if NH_4Cl is added into soluble meta-aluminate and boiled.

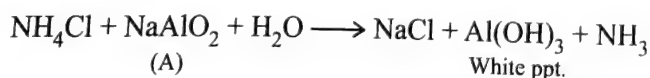


ILLUSTRATION 8.13

Light green solution of (A) does not give blue coloured ppt. with $\text{K}_4[\text{Fe}(\text{CN})_6]$ but on adding a drop of HNO_3 , blue ppt. (B) appears. However, (A) gives blue colour (C) with $\text{K}_3[\text{Fe}(\text{CN})_6]$. Explain the formation of (B) and (C). Identify (A) if (A) also gives white ppt. with AgNO_3 solution.

Sol. (A): FeCl_2

(B): $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$, Prussian blue

(C): $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$, Turnbull's blue

ILLUSTRATION 8.14

Identify (A), (B), (C) and (D) and explain reactions.

(A) (green coloured salt) + $\text{K}_2\text{Cr}_2\text{O}_7$ + conc. $\text{H}_2\text{SO}_4 \xrightarrow{\Delta}$ (B)

(B) (reddish brown gas) + $\text{NaOH} \longrightarrow$ (C)
(yellow coloured solution)

(C) + $(\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow$ (D) (yellow ppt.)

(A) + $\text{NaOH} + \text{Br}_2$ water $\xrightarrow{\Delta}$ (C)

(C) + $(\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\Delta}$ (D)

Sol. (A): CrCl_3

(B): CrO_2Cl_2 [by chromyl-chloride test of Cl^{\ominus}]

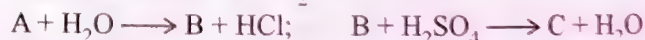
(C): Na_2CrO_4

(D): PbCrO_4

ILLUSTRATION 8.15

- a. (A) (yellow coloured solution) changes to light green coloured solution (B) on passing H_2S gas. (A) and (B) both give white ppt. with BaCl_2 solution, insoluble in conc. HCl . (A) gives blue coloured ppt. (C) with $\text{K}_4[\text{Fe}(\text{CN})_6]$. B does not. What are (A), (B) and (C)?

- b. Identify A, B, C and D in the following reactions:



Sol.

a. (A): FeCl_3 (B): FeCl_2

(C): $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$, Prussian blue

b. $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \xrightarrow{\Delta} 2\text{AlCl}_3 + 3\text{CO}$
Bauxite (A)

$\text{AlCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + 3\text{HCl}$
(A) (B)

$2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O}$
(B) (C)

$\text{Al}(\text{OH})_3 + \text{NaOH} \longrightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O}$
(B) (D)

Filtrate (III)

 $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$
 Pass H_2S gas

 (Centrifugate (IV))
 (Used for subsequent
 group analysis)

 Residue (group IV)
 (CoS , NiS , ZnS , MnS)

 dil. HCl , shake
 well, allow to
 stand, filter

 Residue
 (Black, NiS and CoS)

 Treat with aqua regia,
 evaporate to dryness,
 extract with water

 Filtrate
 (MnCl_2 , ZnCl_2)

 Boil to expel H_2S gas cool.
 Add NaOH soln. (excess) +
 H_2O_2 soln. Boil and filter

 Residue (Brown)
 ($\text{MnO}_2 \cdot x\text{H}_2\text{O}$)

 Dissolve in
 conc. HNO_3

 and divide
 in two parts.

 i. I Part + H_2O_2 ,
 boil and cool.

 Add sodium
 bismuthate

 solid. Stir,
 allow to settle

 → Purple soln.
 (HMnO_4)

 Mn^{2+} confirmed.

 ii. II part + $\text{PbO}_2(\text{s})$.

 Boil and cool.
 → Purple soln.

 Mn^{2+} confirmed.

Divide in two parts

 i. I Part + CH_3COOH

 + pass H_2S

 → white ppt. (ZnS)

 Zn^{2+} confirmed.

 ii. II part +
 CH_3COOH
 + $\text{K}_4\text{Fe}(\text{CN})_6$
 → bluish white ppt.

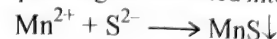
 Zn^{2+} confirmed.

 Filtrate
 (Na_2ZnO_2)

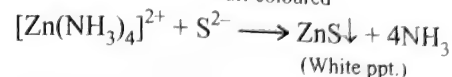
 iii. Black ppt. (salt green) of NiS

 iv. Black ppt. (salt dark brownish black) of CoS

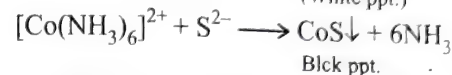
 v. Addition of ammonia (i.e. conc. NH_4OH) converts these
 cations except Mn^{2+} into soluble amino complexes.

 vi. The ammoniacal solution containing Mn^{2+} and these amino
 complexes get converted into sulphides when H_2S is passed.


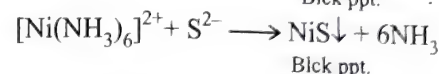
Buff coloured



(White ppt.)

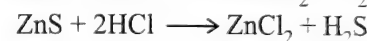


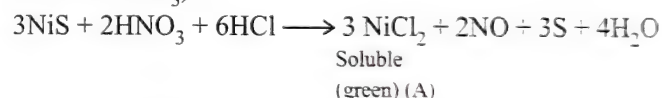
Black ppt.



Black ppt.

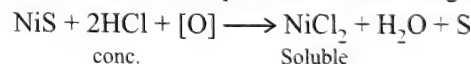
 vii. Ammoniacal medium increases ionisation of H_2S , hence
 higher $[\text{S}^{2-}]$ will precipitate Zn^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} as
 sulphides (having higher K_{sp} values).

 viii. In dil. HCl , NiS and CoS are insoluble, whereas MnS and
 ZnS are soluble.

 Ni^{2+} :

 i. NiS is soluble in aqua regia (3 parts of conc. HCl and 1 part
 of conc. HNO_3)


Soluble

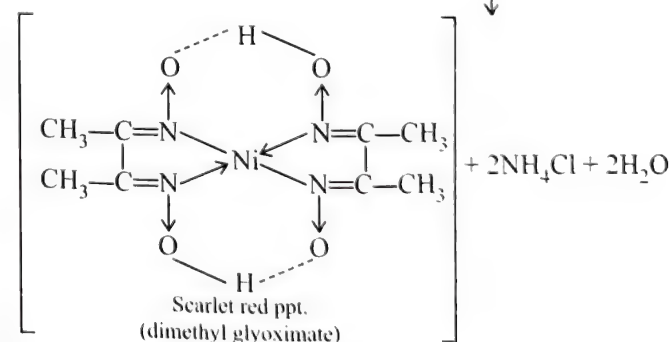
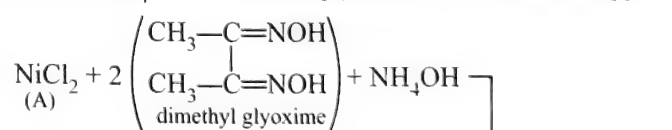
(green) (A)

 or in conc. HCl in presence of oxidising agent like KIO_3


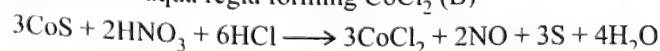
conc.

Soluble

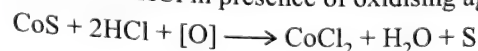
(green) (A)

 ii. (A) + NH_4OH + dimethylglyoxime → scarlet red ppt.

 Scarlet red ppt.
 (dimethyl glyoximate)

 Co^{2+} :

 Co^{2+} is soluble in aqua regia forming CoCl_2 (B)


Soluble (B)

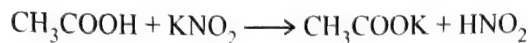
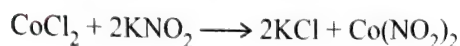
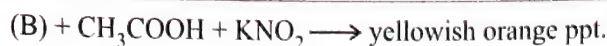
 or in conc. HCl in presence of oxidising agent like KIO_3


8.15.1 Chemical Reactions Involved

 Filtrate of group III + $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl} \xrightarrow{\Delta}$ Pass H_2S gas

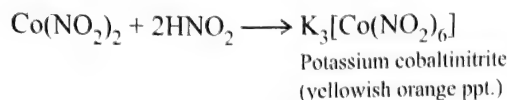
 i. White ppt. (salt colourless) of ZnS

 ii. Buff coloured ppt. (salt light pink) of MnS

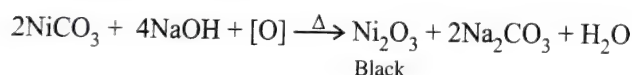
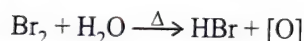
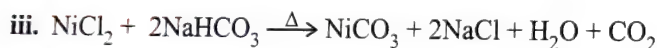
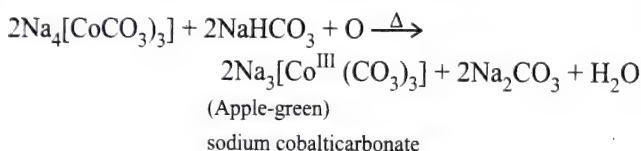
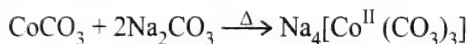
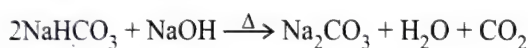
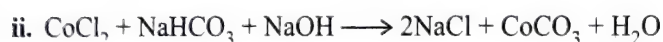
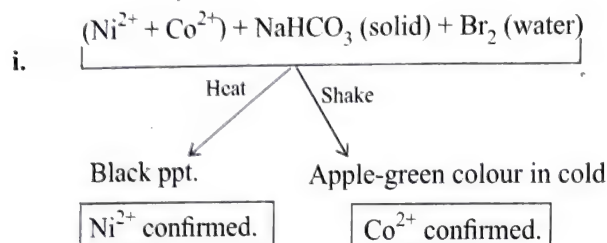


II

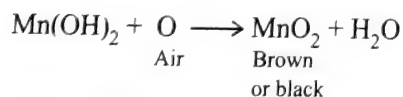
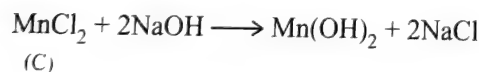
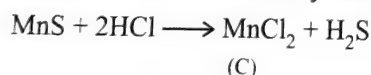
III



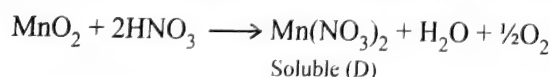
Palit's test: Co^{2+} and Ni^{2+} can be analysed in presence of each other as follows:



iv. Mn^{2+} MnS (buff coloured ppt.) are soluble in dil. HCl , by addition of excess of $NaOH$ gives $Mn(OH)_2$ ppt. which changes to brown / black by atmospheric O_2 .

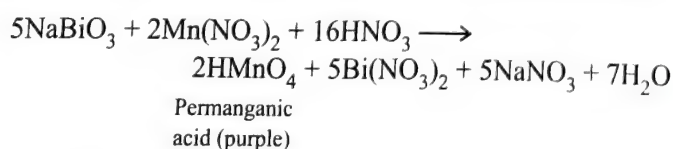


MnO_2 or $Mn(OH)_2$ ppt. + conc. $HNO_3 \longrightarrow$ ppt. dissolves

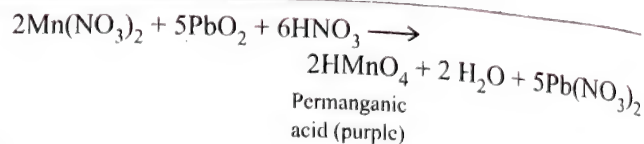


Divide in two parts:

i. (D) + H_2O_2 and sodium bismuthate \longrightarrow purple solution

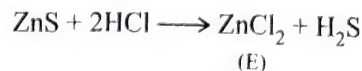


ii. (D) + $PbO_2 \longrightarrow$ Purple solution.

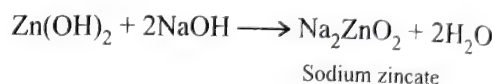
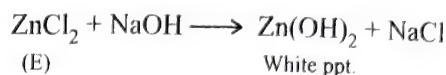


Zn^{2+} :

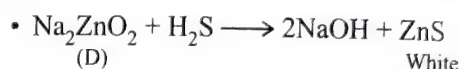
ZnS ppt. (white) are soluble in dil. HCl .



(E) + $NaOH \longrightarrow$ white ppt. soluble in excess of $NaOH$.



• (E) + Pass $H_2S \longrightarrow$ White ppt. of ZnS reappears



• (E) + $CH_3COOH + K_4[Fe(CN)_6] \longrightarrow$ bluish white ppt.

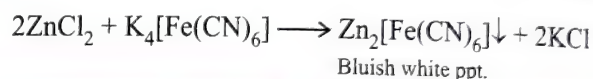


ILLUSTRATION 8.16

(A) (colourless solution) gives white ppt. (B) with $NaOH$ solution but ppt. dissolves in excess of $NaOH$ forming (C). (C) does not give ppt. with H_2S but on boiling with NH_4Cl , white ppt. (B) appears. (A) also gives yellow ppt. with $AgNO_3$. Identify (A), (B) and (C).

Sol. (A): $AlBr_3$ (B): $Al(OH)_3$
(C): $NaAlO_2$

ILLUSTRATION 8.17

Test tube (A) contains aqueous zinc acetate solution while test tube (B) contains aq. zinc chloride solution. What happens if H_2S gas is passed into each solution?

Sol. (A) $Zn(CH_3COO)_2 + H_2S \longrightarrow ZnS + CH_3COOH$
(B) $ZnCl_2 + H_2S \longrightarrow ZnS + 2HCl$

ZnS is precipitated in (A).

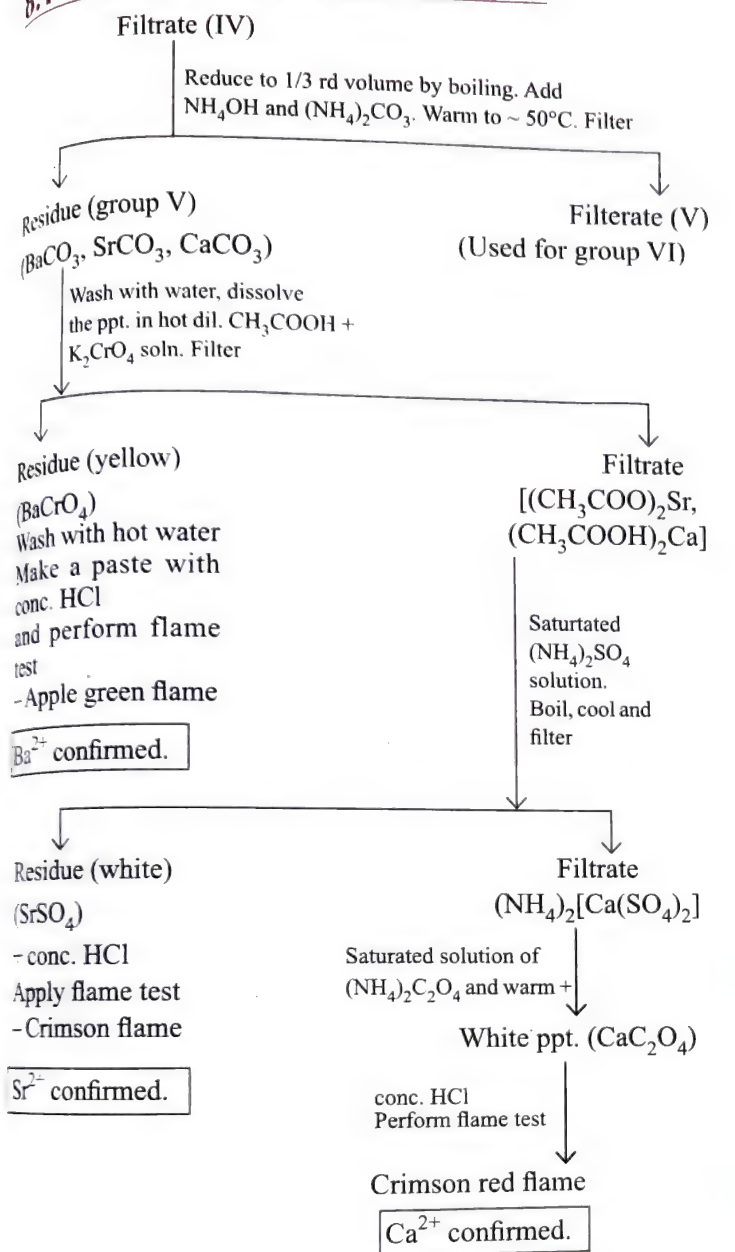
In (B) HCl is formed which dissolves ZnS .

ILLUSTRATION 8.18

Colourless solution of (A) gives white ppt. (B) with $AgNO_3$ soluble in aqueous NH_3 . (A) also gives white ppt. (C) with $NaOH$ soluble in excess of it forming (D). (D) gives white ppt. (E) with H_2S . Identify (A), (B), (C), (D) and (E).

Sol. (A): $ZnCl_2$ (B): $AgCl$
(C): $Zn(OH)_2$ (D): $NaZnO_2$
(E): ZnS

8.16 ANALYSIS OF GROUP V



vi. Filtrate (B) obtained after separating BaCrO_4 , may contain $(\text{CH}_3\text{COO})_2\text{Sr}$, $(\text{CH}_3\text{COO})_2\text{Ca}$ soluble form.

vii. $(\text{B}) + (\text{NH}_4)_2\text{SO}_4 \xrightarrow{\Delta}$ white ppt. (SrSO_4)

viii. $(\text{CH}_3\text{COO})_2\text{Sr} + (\text{NH}_4)_2\text{SO}_4 \rightarrow \text{SrSO}_4 \downarrow + (\text{CH}_3\text{COO})\text{NH}_4$
White ppt.

ix. **Flame test:** By using a paste of SrSO_4 with conc. HCl
Crimson flame

Sr^{2+} confirmed.

x. Filtrate obtained after separating SrSO_4 , may contain

Ca^{2+} as $(\text{NH}_4)_2[\text{Ca}(\text{SO}_4)_2]$ (C)

$(\text{CH}_3\text{COO})_2\text{Ca} + 2(\text{NH}_4)_2\text{SO}_4 \rightarrow (\text{NH}_4)_2[\text{Ca}(\text{SO}_4)_2] + (\text{CH}_3\text{COO})\text{NH}_4$

xi. $(\text{C}) + (\text{NH}_4)_2\text{C}_2\text{O}_4 \xrightarrow{\text{warm}}$ white ppt. (CaC_2O_4)

$(\text{NH}_4)_2[\text{Ca}(\text{SO}_4)_2] + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{CaC}_2\text{O}_4 \downarrow + (\text{NH}_4)_2\text{SO}_4$
Ammonium oxalate White ppt.

xii. **Flame test:** By using a paste of CaC_2O_4 with conc. HCl
Crimson red flame

Ca^{2+} confirmed.

ILLUSTRATION 8.19

$\text{MCl}_2 + \text{K}_2\text{CrO}_4 \rightarrow$ yellow ppt.

What can be MCl_2 :

- If it is soluble in hot water?
- If it gives green colour in flame?

Sol. (A): PbCl_2
(B): BaCl_2

ILLUSTRATION 8.20

(A) (colourless) $\xrightarrow{\Delta}$ (B) (residue) + (C) (gas) + (D) gas

$\downarrow \text{H}_2\text{O}$

Solution of (B) $\xrightarrow{(D)}$ milky

(A) gives brick red colour in flame and decolourises $\text{MnO}_4^-/\text{H}^+$. Gas (C) burns with blue flame. Identify (A), (B), (C) and (D).

Sol. (A): CaC_2O_4 (B): CaO
(C): CO (D): CO_2

ILLUSTRATION 8.21

CaSO_4 is insoluble but is not precipitated when excess of $(\text{NH}_4)_2\text{SO}_4$ is added to CaCl_2 explain.

Sol. $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4 \rightarrow (\text{NH}_4)_2[\text{Ca}(\text{SO}_4)_2]$

8.16.1 CHEMICAL REACTIONS INVOLVED

Filtrate of group (V)

i. Filtrate of group (IV) $\xrightarrow[\text{(ii) } (\text{NH}_4)_2\text{CO}_3]{\text{(i) boil off } \text{H}_2\text{S}}$ white ppt.

ii. BaCO_3 , CaCO_3 , SrCO_3 , appears as white ppt.

iii. Dissolve the white ppt. in CH_3COOH . Heat
 $\text{MCO}_3 + \text{CH}_3\text{COOH} \xrightarrow{\Delta} (\text{CH}_3\text{COOH})_2\text{M} + \text{H}_2\text{O} + \text{CO}_2$
($\text{M} = \text{Ba}^{2+}$, Ca^{2+} , Sr^{2+}) Soluble (A)

The carbonates dissolve in CH_3COOH forming acetates.

iv. (A) + $\text{K}_2\text{CrO}_4 \rightarrow$ yellow ppt. (BaCrO_4)
 $(\text{CH}_3\text{COOH})_2\text{Ba} + \text{K}_2\text{CrO}_4 \rightarrow \text{BaCrO}_4 \downarrow + 2\text{CH}_3\text{COOK}$
Yellow

v. **Flame test:** By using a paste of BaCrO_4 with conc. HCl , apple-green flame

Ba^{2+} confirmed.

8.17 ANALYSIS OF GROUP VI

Centrifugate (V)

Boil off NH_4^+ (if present)
Evaporate to dryness extract with water. Centrifuge

i. Residue (white)
(Mg^{2+} salts)

Dissolve in dil. HCl
Add NH_4OH (till alkaline)
+ Na_2HPO_4 soln.
Shake well and scratch the sides of test tube

White crystalline ppt
 $\text{Mg}(\text{NH}_4)_2\text{PO}_4$

Mg^{2+} confirmed.

ii. Cobalt-nitrate or (Rinmann's) Charcoal cavity test:

A pink mass is formed.
 Mg^{2+} confirmed.

Filterate (A)
(K^+ salts)

Divide in two parts :

i. I Part + CH_3COOH + sodium cobaltinitrite solution.

Yellow ppt. obtained on standing of $\text{K}_3[\text{Co}(\text{NO}_2)_6]$

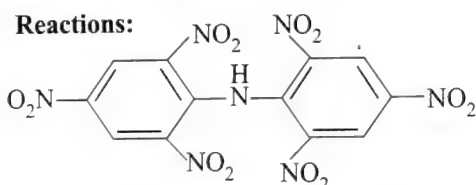
K^+ confirmed.

ii. Spot test:

II Part + Dipicrylamine reagent

Orange red-ppt. uneffected by few drops of dil. HCl.

K^+ confirmed.



Note: Dipicrylamine reagent (Hexa-nitro-diphenylamine) is prepared by dissolving 0.2g of dipicrylamine in 20 mL of 0.1 N Na_2CO_3 and filtering the cooled liquid.

Note: H atom of NH group is replaceable by metals.
 NH_4^+ must be absent
 Mg^{2+} does not interfere.

iii. Flame test: A crimson colour using cobalt blue glass.

K^+ confirmed.

8.17.1 CHEMICAL REACTIONS INVOLVED

For Mg^{2+} ion:

Filtrate of group V + NH_4OH + $\text{Na}_2\text{HPO}_4 \longrightarrow$ fine Crystalline ppt. on scratching the side of the test tube

$$\text{MgCl}_2 + \text{NH}_4\text{OH} + \text{Na}_2\text{HPO}_4 \longrightarrow \text{Mg}(\text{NH}_4)\text{PO}_4 \downarrow + 2\text{NaCl} + \text{H}_2\text{O}$$

White ppt.

For K^+ ion:

Filtrate (A) + CH_3COOH + Sodium cobaltinitrite solution (in excess)

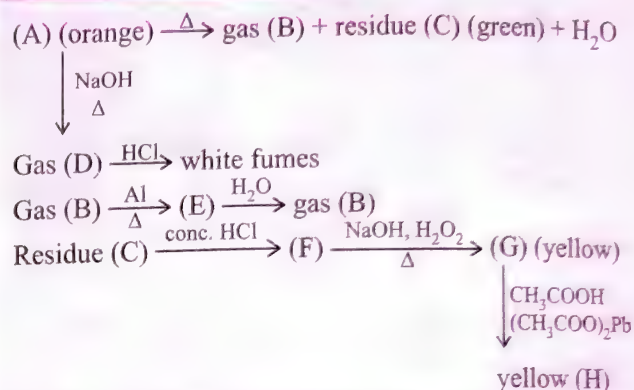
\longrightarrow yellow ppt. on standing.

$$\text{Na}_3[\text{Co}(\text{NO}_2)_6] + 3\text{KCl} \longrightarrow \text{K}_3[\text{Co}(\text{NO}_2)_6] \downarrow + 3\text{NaCl}$$

(excess) White ppt. (Potassium cobaltinitrite)

Potassium cobaltinitrite is insoluble in CH_3COOH .
(NH_4^+) salts give a similar test with sodium cobaltinitrite and therefore must be completely eliminated before doing the test for K^+ ions.

ILLUSTRATION 8.22

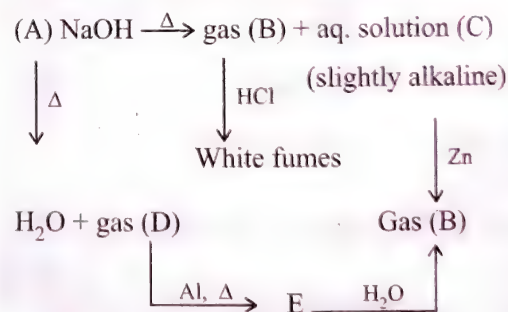


Identify (A) to (H) and explain reactions.

Sol. (A): $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (B): N_2 (C): Cr_2O_3
(D): NH_3 (E): AlN (F): CrCl_3
(G): Na_2CrO_4 (H): PbCrO_4

ILLUSTRATION 8.23

Identify (A), (B), (C), (D) and (E).



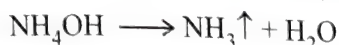
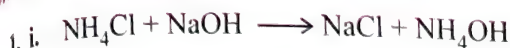
Sol. (A): NH_4NO_2 (B): NH_3
(C): NaNO_2 (D): N_2 (E): AlN

8.18 ANALYSIS OF ZERO GROUP (NH_4^+)

S.No.	Experiment	Observation	Inference
I. i.	Mixture + 1–2 mL of NaOH soln. Heat	Smell of NH_3 observed	NH_4^+ may be present
ii.	Bring a glass rod dipped in conc. HCl at the mouth of test tube	White dense fumes (NH_4Cl) are observed	—

2. Pass the gas evolved in above test through Nessler's reagent or Water extract of the mixture + NaOH soln. + Nessler's reagent	Brown colour ppt. is obtained	NH_4^+ confirmed
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8.18.1 CHEMICAL REACTIONS INVOLVED



(White fumes)

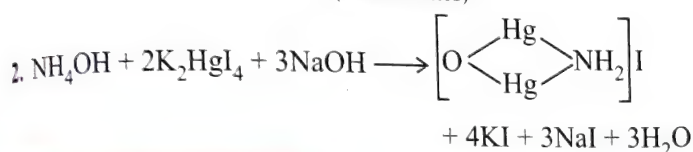
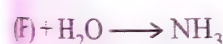
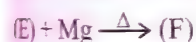
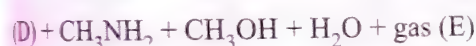
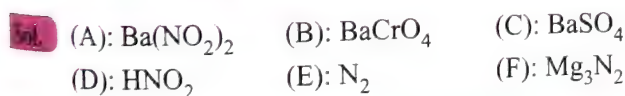


ILLUSTRATION 8.24

Colourless salt (A) gives apple-green flame with conc. HCl. (A) on reaction with dil. H_2SO_4 gives light brown fumes (D) turning KI-starch paper blue.

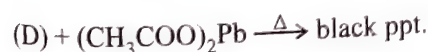
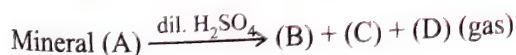


Identify (A) to (F) and explain reactions.

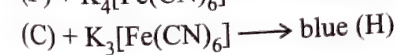
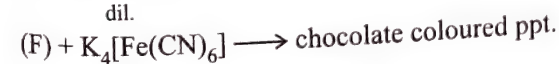
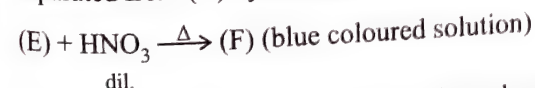


CONCEPT APPLICATION EXERCISE 8.1

1. Identify (A) to (H).



separated from (C) by filtration



2. An aqueous solution of salt (A) gives a white crystalline precipitate (B) with NaCl solution. The filtrate gives

a black precipitate (C) when H_2S is passed through it. Compound (B) dissolves in hot water and the solution gives yellow precipitate (D) on treatment with potassium iodide and on cooling. The compound (A) does not give any gas with dilute HCl but liberates a reddish brown gas on heating. Identify the compounds (A) to (D) giving the involved equations.

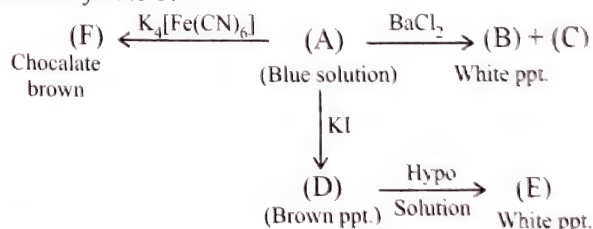
3. A white amorphous powder (A) when heated gives a colourless gas (B), which turns lime water milky and the residue (C) which is yellow when hot but white when cold. The residue (C) dissolves in dilute HCl and the resulting solution gives a white precipitate on addition of potassium ferrocyanide solution. (A) dissolves in dilute HCl with the evolution of a gas which is identical in all respects with (B). The solution of (A) as obtained above gives a white precipitate (D) on addition of excess of NH_4OH and on passing H_2S . Another portion of this solution gives initially a white precipitate (E) on addition of NaOH which dissolves in excess of it. Identify (A) to (E).

4. Compound (A) is a light green crystalline solid. It gives the following tests:

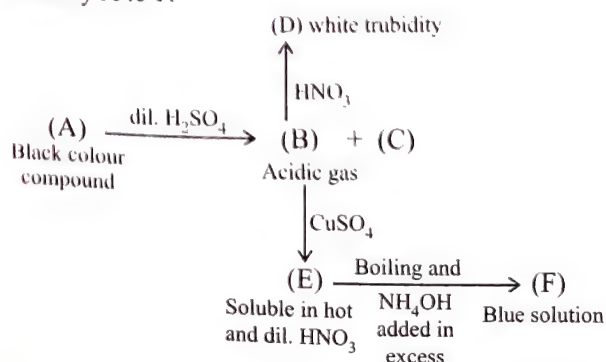
- It dissolves in dilute sulphuric acid. No gas is produced.
- A drop of KMnO_4 is added to the above solution. The pink colour disappears.
- Compound (A) is heated strongly. Gases (B) and (C) with pungent smell came out. A brown residue (D) is left behind.
- The gas mixture [(B) and (C)] is passed into a dichromate solution. The solution turns green.
- The green solution from step (iv) gives a white precipitate (E) with a solution of barium nitrate.
- Residue (D) from (v) is heated on charcoal in reducing flame, it gives a magnetic substance.

Identify the compounds (A) to (E).

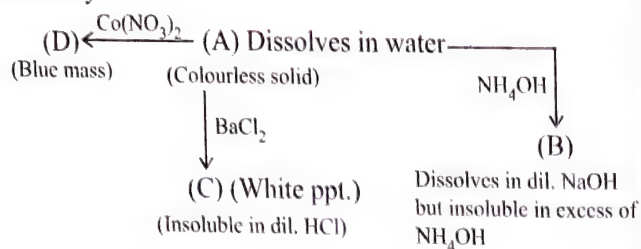
5. Identify A to F.



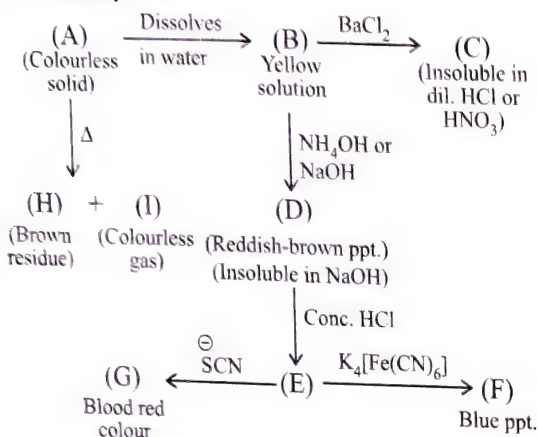
6. Identify A to F.



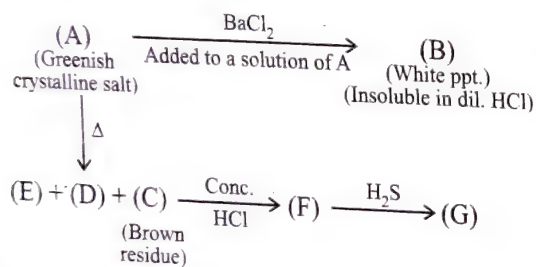
7. Identify A to D.



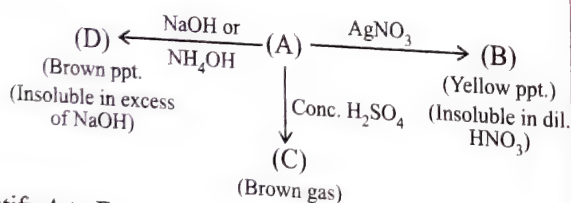
8. Identify A to I.



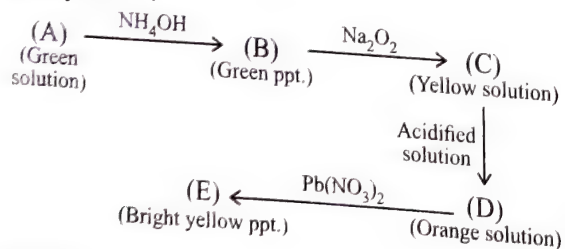
9. Identify A to G.



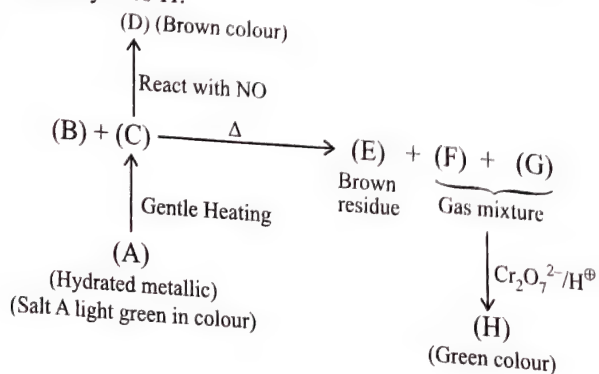
10. Identify A to D.



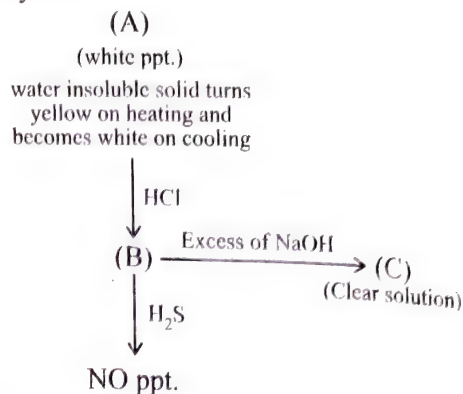
11. Identify A to E.



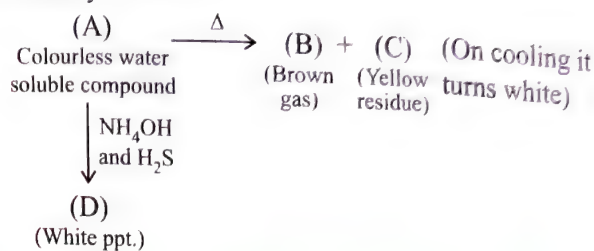
12. Identify A to H.



13. Identify A to C.



14. Identify A to D.



ANSWERS

- (A): CuFeS_2 (B): CuSO_4 (C): FeSO_4
(D): H_2S (E): CuS (F): $\text{Cu(NO}_3)_2$
(G): $\text{Cu}_2[\text{Fe(CN)}_6]$
(H): $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$, Turnbulls blue
- (A): $\text{Pb(NO}_3)_2$ (B): PbCl_2
(C): PbS (D): PbI_2
- (A): ZnCO_3 (B): CO_2
(C): ZnO (D): ZnS
(E): Zn(OH)_2
- (A): $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (B): SO_2 (C): SO_3
(D): Fe_2O_3 (E): BaSO_4
- (A): CuSO_4 (B): BaSO_4 (C): HCl
(D): $(\text{Cu}_2\text{I}_2 + \text{I}_3^-)$ (E): $(\text{Cu}_2\text{I}_2 + \text{I}^- + \text{S}_4\text{O}_6^{2-})$
(F): $\text{Cu}_2[\text{Fe(CN)}_6]$
- (A): FeS (B): H_2S (C): FeSO_4
(D): S (E): CuS
(F): $[\text{Cu(NH}_3)_4](\text{OH})_2$
- (A): $\text{Al}_2(\text{SO}_4)_3$ (B): Al(OH)_3 (C): BaSO_4
(D): $\text{CoO} \cdot \text{Al}_2\text{O}_3$
- (A): $\text{Fe}_2(\text{SO}_4)_3$ (B): $\text{Fe}_2(\text{SO}_4)_3$ solution
(C): BaSO_4 (D): Fe(OH)_3
(E): FeCl_3 (F): $\text{Fe}_4[\text{Fe(CN)}_6]_3$
(G): Fe(SCN)_3 (H): Fe_2O_3 (I): SO_3
- (A): FeSO_4 (B): BaSO_4 (C): Fe_2O_3
(D): SO_2 (E): SO_3 (F): FeCl_3
(G): S
- (A): FeBr_3 (B): AgBr (C): Br_2
(D): Fe(OH)_3
- (A): CrCl_3 (B): Cr(OH)_3 (C): Na_2CrO_4
(D): $\text{Na}_2\text{Cr}_2\text{O}_7$ (E): PbCrO_4

12. (A): $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (B): FeSO_4 (C): $7\text{H}_2\text{O}$
 (D): $\text{Fe}[(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ (E): Fe_2O_3
 (F): SO_2 (G): SO_3
 (H): Cr^{3+} solution
13. (A): ZnO (B): ZnCl_2 (C): Na_2ZnO_2
 14. (A): $\text{Zn}(\text{NO}_3)_2$ (B): NO_2 (C): ZnO
 (D): ZnS

Viva-Voce Questions and Answers

PART-A (Analysis of Anions)

- What is a group reagent?**
Ans. The reagent which is employed in identifying a group of radicals is known as a group reagent.
- Why sodium carbonate extract is used for testing acid radicals?**
Ans. The scheme followed for the systematic analysis of acid radicals is based on sodium salts of acid radicals. Other basic radicals if present may interfere with their salts.
- Can we use sodium bicarbonate in place of sodium carbonate in preparing an extract for detection of anions?**
Ans. No. Metal bicarbonates formed by double decomposition will remain in solution.
- Why is sodium carbonate extract acidified before performing the confirmatory tests for anions?**
Ans. Sodium carbonate extract in addition to the sodium salts of anions contain carbonate also. On heating with the test reagent carbonates of certain metals precipitate which interfere in the detection of acid radicals. Because of this, Na_2CO_3 is decomposed by adding HCl , HNO_3 , H_2SO_4 , depending upon the nature of test.
- Can sodium carbonate extract be used test for CO_3^{2-} ions?**
Ans. No, because it already contains these ions.
- What is lime water?**
Ans. It is a water solution of calcium hydroxide.
- Why does lime water turns milky on bubbling CO_2 gas through it?**
Ans. Initially CaCO_3 (causing milkiness) is formed which disappears due to the formation of $\text{Ca}(\text{HCO}_3)_2$ which $\text{CO}_2(\text{g})$ is passed for long time.
- Name the anions which give brown fumes on reacting with dilute / conc. H_2SO_4 .**
Ans. With dilute H_2SO_4 , NO_2^- ion gives brown fumes. With conc. H_2SO_4 both Br^- and NO_3^- ions give brown fumes.
- Why does a paper soaked in $\text{K}_2\text{Cr}_2\text{O}_7$ solution turn green in the detection of SO_3^{2-} ion?**
Ans. The paper turns green because the SO_2 gas evolved from SO_3^{2-} salt reduces $\text{K}_2\text{Cr}_2\text{O}_7$ to $\text{Cr}_2(\text{SO}_4)_3$ which turns the paper green.
- Can filter paper dipped in silver nitrate solution instead of lead acetate paper be used for testing a sulphide?**
Ans. Yes, a paper dipped in AgNO_3 when exposed to the vapours of H_2S turns black due to the formation of silver sulphide.

$$2\text{AgNO}_3 + \text{H}_2\text{S} \longrightarrow \text{Ag}_2\text{S} + 2\text{HNO}_3$$
- A gas evolved with effervescence on treating a salt with dil. HCl may be CO_2 or SO_3 . How will you distinguish between them?**
Ans. a. SO_2 has a pungent burning sulphur smell, whereas CO_2 is odourless.
 b. SO_2 turns potassium dichromate paper green, whereas CO_2 does not.
- How will you distinguish between carbonate and bicarbonate ions?**
Ans. MgSO_4 gives a white ppt. with carbonate ions in cold solution while a white ppt. is obtained with bicarbonate ions in hot solution only.
 Phenolphthalein gives a pink colour with carbonate ions and no colour is obtained with bicarbonate ions.
- How can sulphide ions be distinguished from sulphite ions?**
Ans. AgNO_3 forms white ppt. with sulphite ions while a black precipitate is obtained with sulphide ions.
 BaCl_2 gives white ppt. with sulphite ions while no ppt. is obtained with sulphide ions.
 FeCl_3 solution gives a red colouration with sulphite ions and a black ppt. is formed with sulphide ions.
- How will you distinguish between sulphate and thiosulphate ions?**
Ans. AgNO_3 gives white ppt. with thiosulphate ions which turns black on standing whereas no ppt. is obtained with sulphate ions.
 FeCl_3 gives purple colour with thiosulphate ions which disappears gradually and no ppt. or colouration is obtained in case of sulphate.
- How will you distinguish between sulphite and sulphate ions?**
Ans. BaCl_2 gives a white ppt. with both sulphite and sulphate ions.
 BaSO_3 is soluble in conc. HCl whereas BaSO_4 is insoluble in conc. HCl .
 FeCl_3 solution gives a red colour with sulphite and no colour is obtained with sulphate.
- How can nitrite ion be distinguished from nitrate ion?**
Ans. Nitrate ion gives a brown ring with FeSO_4 and conc. sulphuric acid. But with nitrite ion a black coloured solution is obtained.
- What is the formula of compound present in brown ring?**
Ans. $3\text{Fe}^{2+} + \text{NO}_3^- + 4\text{H}^+ \longrightarrow 3\text{Fe}^{3+} + \text{NO} + 2\text{H}_2\text{O}$
 $\text{FeSO}_4 + \text{NO} \longrightarrow \text{FeSO}_4 \cdot \text{NO}$ or $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$
- Why is a freshly prepared solution of FeSO_4 used for the detection of nitrate and nitrite?**

Ans. This is because Fe^{2+} ions on long standing are oxidised to Fe^{3+} ions which are not used for the detection of nitrate or nitrite.

19. Why does only the organic layer assure colour and not the aqueous layer when the tests for halides are done?

Ans. Both Br_2 and I_2 are covalent. They have preference for organic layer.

20. What happens when chloride, bromide and iodide are separately heated with conc. H_2SO_4 ?

- Ans. a.** Chloride gives HCl gas which gives thick white fumes with aqueous ammonia.
b. Bromide gives reddish-brown Br_2 vapours.
c. Iodide gives violet vapours of iodine which turns starch paper blue.

21. How do you distinguish between Br^- and NO_3^- ions?

Ans. Treat the salt with conc. H_2SO_4 . Pass the reddish-brown gas evolved through FeSO_4 solution. If it turns black, it is NO_3^- . In case it does not turn black, the anion is Br^- .

22. Given salt is a bromide or iodide. How will you identify it by treating the salt with chlorine water and CS_2 ?

Ans. If CS_2 layer assumes an orange colour, it is Br^- . If CS_2 layer assumes a violet colour, it is I^- .

23. Why does the chromyl chloride test fail with Br^- and I^- ?

Ans. Because both chromyl bromide and chromyl iodide are not volatile in nature.

24. For testing SO_4^{2-} with BaCl_2 solution, why should sodium carbonate not be acidified with too much of conc. HCl .

Ans. In the presence of conc. HCl , BaCl_2 itself will be precipitated. The precipitated BaCl_2 is mistaken as BaSO_4 .

25. Can any other reagent in place of lime water be employed for identification of CO_2 gas?

Ans. Yes, $\text{M}(\text{OH})$ can be employed.

26. At times the solution of lime water appears milky. Comment.

Ans. The lime water lying in the reagent bottle absorbs CO_2 gas from the atmosphere and produces white insoluble CaCO_3 .
 $\text{Ca}(\text{OH})_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}$

27. Name the gas other than CO_2 which also turns lime water milky.

Ans. SO_2 gas also turns lime water milky as insoluble CaSO_3 is produced.

28. Why is it necessary to test for the acid radicals first (with dilute) H_2SO_4 and then with conc. H_2SO_4 ?

Ans. There are some ions like, SO_3^{2-} , S^{2-} , NO_2^- , and CH_3COO^- which can react with dilute/conc. H_2SO_4 whereas ions like Cl^- , Br^- , I^- , NO_3^- , etc. react only with conc. H_2SO_4 .

Now if conc. H_2SO_4 is used first then the anions of both the types will react. Hence, it is desired to test acid radicals first with dilute H_2SO_4 and then with conc. H_2SO_4 .

29. What is chromyl chloride test? Why is it so named?

Ans. Chlorides of metals other than heavy ones, e.g. Hg^{2+} , on reacting with conc. H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ produce orange colour vapours, which on reacting with NaOH and lead acetate produce yellow ppt. of PbCrO_4 .

Orange colour vapours are that of chromyl chloride, CrO_2Cl_2 , hence the test is so named.

30. Sodium carbonate extract is acidified with HNO_3 only in the identification of halides. Comment.

Ans. HCl and H_2SO_4 are not used, as the acids react with the test reagent AgNO_3 and form ppt. of AgCl and Ag_2SO_4 respectively. Because of this only HNO_3 is used for the purpose.

PART-B (Dry Tests)

31. Why do salts of the following ions Cu^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Na^+ and K^+ impart colour to the flame?

Ans. This is due to the fact that the chlorides of these are volatile and at higher temperature they ionise giving respective cations. Since the energy of bunsen flame is constant, different elements are excited to different levels due to difference in their ionisation energies. When these excited electrons return to their original energy level, they emit the same amount of energy absorbed during excitation in the form of electromagnetic radiation which appears in the visible region of the spectrum, thereby imparting a characteristic colour to flame.

32. Why is HCl employed in flame test?

Ans. Only the volatile compounds of cations impart colour to the flame. Only metal chlorides are volatile whereas their sulphates, nitrates etc. are not. Thus, HCl is used to convert cations into their volatile chlorides.

33. What type of flame is employed to perform the flame test? How is it obtained?

Ans. A non-luminous flame is employed to perform the test. It is obtained by keeping the holes of the burner open.

34. Why is a green flame not obtained in the case of barium sulphate or phosphate?

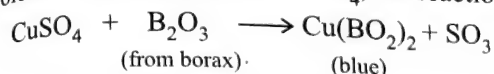
Ans. Both barium sulphate and phosphate are insoluble and cannot be easily converted into chlorides. Therefore, the green flame is either indistinct or visible with difficulty.

35. Can we perform the charcoal cavity test without the addition of fusion mixture (Na_2CO_3 and K_2CO_3) with the carbonate of metals?

Ans. Yes, we can directly perform the charcoal cavity test without the addition of fusion mixture because the latter simply converts the substances into carbonates in fused state. Carbonates of metals on heating in the charcoal cavity are reduced to metallic state.

36. Why do we not perform borax bead test with the white salt?

Ans. This test is applied for the identification of the cations of the coloured salt only because the borax forms the corresponding metaborates which possess characteristic colour. For example, with CuSO_4 , the reaction is



37. What is the composition of the bead obtained when borax is heated in the flame?

Ans. It consists of a mixture of sodium metaborate and boric anhydride.

38. Why is a small quantity of mixture used in the borax bead test?

Ans. To avoid the formation of dark and opaque bead which in subsequent treatment cannot be recognised easily.

39. Name the cations which can be identified by flame test.

Ans. Cu^{2+} – Bright green, Ba^{2+} – Apple green
 Ca^{2+} – Brick red, Sr^{2+} – Crimson
 K^+ – Lilac

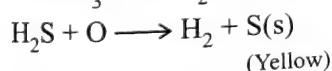
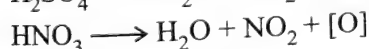
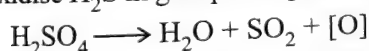
PART-C (Analysis of Cations)

40. Why is it necessary to prepare original solution for the detection of basic radicals?

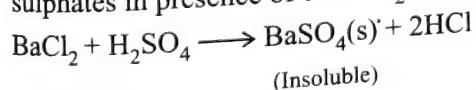
Ans. The detection of basic radicals depends on the behaviour of ions in solution. For this purpose the preparation of original solution is necessary as it furnishes free ions in solution.

41. Why do we not prefer to prepare original solution in conc. H_2SO_4 or conc. HNO_3 ?

Ans. It is not advisable to prepare original solution in conc. HNO_3 or conc. H_2SO_4 because these are oxidising agents and they oxidise H_2S in group II to produce a yellow ppt. of sulphur.



Also Pb^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} are precipitated as their insoluble sulphates in presence of conc. H_2SO_4 .



42. What is solubility product? Explain its importance in qualitative analysis.

Ans. The ionic product in a saturated solution of an electrolyte at a given temperature is always a constant quantity and is termed as solubility product. Whenever in a solution the ionic product exceeds the solubility product, the precipitation occurs due to the supersaturation of solution.

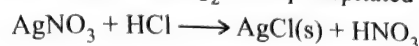
43. What is the basis of classification of cations into different group?

Ans. The different cations are classified under six groups depending upon the difference in the solubilities of their

chlorides, sulphide hydroxides and carbonates at different pH values.

44. Why are only Pb^{2+} , Ag^+ and Hg_2^{2+} ions precipitated in group I?

Ans. Out of all the chlorides, those of Pb^{2+} , Ag^+ and Hg_2^{2+} are insoluble. HCl is the reagent of group I. Thus, chlorides of Pb^{2+} , Ag^+ and Hg_2^{2+} are precipitated in group I.



(White ppt.)

Other cations remain in solution because their chlorides are soluble.

45. Why is lead placed in group I as well as in II?

Ans. This is due to fact that lead is not completely precipitated in group I as lead chloride. PbCl_2 is also soluble in hot water. Therefore, the lead which escapes precipitation in group I as PbCl_2 is precipitated in the group II as PbS .

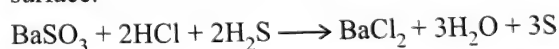
46. Is it necessary to acidify a solution before group II cations are precipitated with H_2S ?

Ans. Yes, because for the precipitation of cations of group II only small concentration of sulphide ions (S^{2-}) is required. This condition is achieved by passing H_2S gas in a solution acidified with HCl (dil.). Due to common ion effect, concentration of S^{2-} ions decreases as presence of hydrochloric acid suppresses the ionisation of H_2S , resulting only in the precipitation of sulphides of group II metals.

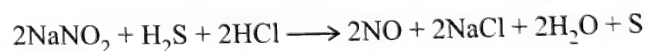
Other metal sulphides remain in solution as they require higher concentration of S^{2-} ions for their precipitation.

47. Give the reason for the formation of a light yellow or white ppt. in the group II even if it may not be because of some metal ion.

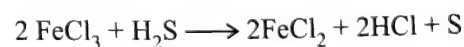
Ans. Yellow or white ppt. is formed due to the oxidation of H_2S gas by some oxidising agents to sulphur which floats on the surface.



(yellow)



(yellow)



(yellow)

48. Why do we prefer HCl for preparing solutions of cations?

Ans. Because most of the salts are soluble in HCl except those of group I.

49. Is it advisable to use conc. HCl in place of dilute HCl for preparing original solution.

Ans. Conc. HCl can be used but to ensure the precipitation of Pb^{2+} as PbCl_2 , the solution is prepared in dil. HCl as PbCl_2 dissolves in conc. HCl due to complex formation.

50. Why is it essential to boil off H_2S gas before proceeding to group III.

Ans. Otherwise the sulphides of group IV will also be precipitated along with precipitate of group III.

51. Can the solution be acidified with HNO_3 in group II before passing H_2S gas?

Ans. No, HNO_3 being oxidising in nature oxidises H_2S gas to form colloidal sulphur which makes the analysis complicated.

52. What can it be, if the precipitate of group I is soluble in hot water and insoluble in cold water?

Ans. PbCl_2

53. Why is H_2SO_4 never employed for preparing original solution for the identification of cations?

Ans. Ba^{2+} , Sr^{2+} and Pb^{2+} are precipitated as insoluble sulphates.

54. Group I filtrate is made moderately acidic before proceeding to group II. Explain.

Ans. Precipitation of the sulphide can occur only when the ionic product $[\text{M}^{2+}][\text{S}^{2-}]$ exceeds the solubility product of the sulphide, MS.

In the presence of acid, the ionisation of H_2S is suppressed due to the increased concentration of H^+ . As a result, there are only few S^{2-} ions in solution which are enough to precipitate only group II cations as sulphides, e.g. CuS , PbS , etc.

But for the precipitation of CdS , the concentration of S^{2-} is not enough. Hence the concentration of (H^+) should be further decreased by diluting the solution so that the H_2S is ionised extensively. As a result S^{2-} ions are made available in sufficient quantity which can precipitate the Cd^{2+} ions. i.e. ionic product $[\text{Cd}^{2+}][\text{S}^{2-}]$ exceeds solubility product of CdS .

55. What is the use of adding nitric acid in the precipitation of group III cations as hydroxides.

Ans. Nitric acid is useful in the oxidation of ferrous salts to ferric salts in group III.



56. Why do we add excess of NH_4Cl and NH_4OH in the precipitation of group III cations?

Ans. The solubility product of hydroxides of cations of group III is extremely low.

NH_4Cl suppresses the ionisation of NH_4OH to a great extent due to common ion effect. As a result, low concentration of OH^- is made available for precipitating group III cation hydroxides.

Other hydroxides remain in solution as they require higher concentration of OH^- ions for precipitation as hydroxides.

57. Why is it essential to oxidise ferrous salt to ferric salt in group III?

Ans. This is because the ferrous salts are not completely precipitated as $\text{Fe}(\text{OH})_2$ in the presence of NH_4Cl on the addition of NH_4OH and thus iron will also be precipitated in the group IV as FeS on passing H_2S .

Therefore, to precipitate iron completely in the group III, it is necessary to oxidise ferrous salt to ferric salt.

58. Can NH_4Cl be replaced by any other ammonium salt for the precipitation of group III cations?

Ans. Yes, NH_4NO_2 can be used in place of NH_4Cl for the precipitation of group III cations. Ammonium sulphate cannot be used as it may precipitate Ca^{2+} , Ba^{2+} and Sr^{2+} as insoluble sulphates.

59. How will you distinguish between ferrous and ferric salts?

Ans. Ammonium sulphocyanide does not give any colouration with ferrous salt while it gives a blood-red colour with ferric salt.

Potassium ferricyanide produces a blue ppt. with ferrous salt while a red colouration is obtained with ferric salt.

60. Can we add NH_4OH first and NH_4Cl later in the analysis of group III cations?

Ans. No, the function of NH_4Cl is to suppress ionisation of NH_4OH and thereby it prevents precipitation of $\text{Zn}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, etc.

In case NH_4OH is added first these hydroxides will be immediately precipitated. Addition of NH_4Cl afterwards will be of no use.

61. Can we use NaCl and NaOH in place of NH_4Cl and NH_4OH in the group III cation precipitation.

Ans. No, NaOH is a strong base and highly ionised. Even in the presence of NaCl , $[\text{OH}^-]$ will be large enough to precipitate $\text{Zn}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, etc.

62. Why are Zn , Mn , Ni , Co not precipitated in the group III as hydroxides?

Ans. The solubility products of hydroxides of Zn , Mn , Ni and Co are very high. For this purpose they require high concentration of OH^- ions. This is not possible in the group III as NH_4Cl suppresses the ionisation of NH_4OH due to common ion effect.

63. Why are the group IV cations not precipitated as sulphides on passing H_2S gas through group II solution?

Ans. For the precipitation of cations of group IV, a very large concentration of sulphide ions (S^{2-}) is required which is not available in the group II as the ionisation of H_2S is suppressed by HCl (common ion effect).

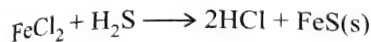
In precipitating the cations of group IV, high concentration of S^{2-} ions is required as OH^- ions released by NH_4OH unite with H^+ ions given by H_2S . Thus the solubility product is exceeded and the cations of group IV are precipitated as ZnS , NiS , MnS and CoS .

64. Why is a brownish ppt. obtained in group III even if iron, aluminium and chromium are absent?

Ans. When NH_4Cl is not present in sufficient amount, Mn is precipitated as $\text{MnO}_2 \cdot \text{H}_2\text{O}$ which is brown in colour.

65. Why sometimes, a black coloured precipitate obtained in group IV even if nickel and cobalt ions are absent?

Ans. A black coloured precipitate is obtained in the group IV due to the incomplete removal of iron in group III. Iron escapes precipitation in group III due to lack of enough NH_4OH . Fe^{+3} is reduced to Fe^{2+} by H_2S which finally gets precipitated as FeS (black) in group IV even when both Co and Ni are absent.

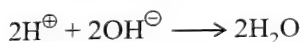
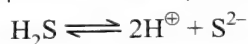
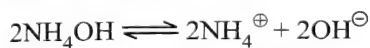


(Black ppt.)

66. Why excess of NH_4OH is used in precipitating the sulphides of group IV cations?

Ans. The solubility product of group IV radicals is greater than that of group II ions. Therefore, a higher concentration of S^{2-} ions is required to precipitate group IV ions as their sulphides. Now to get a higher concentration of S^{2-} ions, H_2S gas is passed in presence of NH_4OH . The OH^- ions from NH_4OH neutralise the H^+ ions from H_2S to form undissociated water molecules. The removal of H^+ ion causes more H_2S to dissociate or ionise, thus increasing the concentration of S^{2-} ions and so the product $[\text{M}^{2+}][\text{S}^{2-}]$ exceeds the solubility products of the sulphides of Zn, Mn, Ni and Co and hence they are precipitated.

(M = Zn, Mn, Co or Ni)



67. Why sometimes colloidal precipitate is obtained in group IV? Comment.

Ans. To prevent the colloidal precipitate, ammonium chloride must be present in large amount. H_2S should not be passed for long.

68. Why is NH_4Cl essential in the precipitation of group V cations?

Ans. Ammonium chloride prevents the precipitation of Mg^{2+} as MgCO_3 by the group reagent $(\text{NH}_4)_2\text{CO}_3$ by lowering down its dissociation into NH_4^+ and CO_3^{2-} ions.

69. Does the excess of NH_4Cl affect the precipitation of group V cations by $(\text{NH}_4)_2\text{CO}_3$?

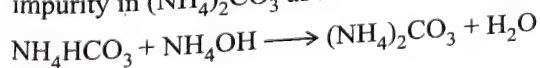
Ans. Yes, the concentration of CO_3^{2-} is decreased because the common ion NH_4^+ suppresses the ionisation of $(\text{NH}_4)_2\text{CO}_3$.

70. Why are all aqueous solutions of the cobaltous salts pink?

Ans. All aqueous solutions of cobaltous salts are pink due to the formation of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions.

71. At times NH_4OH is added before adding $(\text{NH}_4)_2\text{CO}_3$ to precipitate group V cations. Explain.

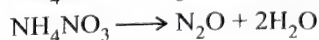
Ans. Ammonium hydroxide reacts with bicarbonate present as impurity in $(\text{NH}_4)_2\text{CO}_3$ as follows:



The presence of bicarbonate is undesirable as the bicarbonates of Ba, Sr and Ca are soluble in water.

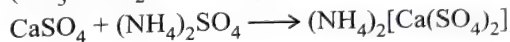
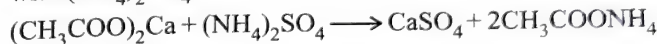
72. How will you remove the excess of NH_4Cl before adding $(\text{NH}_4)_2\text{CO}_3$ for the precipitation of group V?

Ans. NH_4Cl is removed by treating the filtrate from group IV with conc. HNO_3 . On heating to dryness, ammonium chloride is decomposed according to the following equations:



73. Why is CaSO_4 not precipitated on adding ammonium sulphate to a solution containing Ca^{2+} and Sr^{2+} ions?

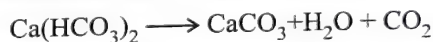
Ans. CaSO_4 is not precipitated due to the formation of a complex with $(\text{NH}_4)_2\text{SO}_4$.



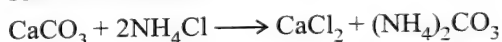
(soluble complex)

74. At times warming is suggested while precipitating group V cations. Explain.

Ans. The impurity of bicarbonate ion in $(\text{NH}_4)_2\text{CO}_3$ forms soluble bicarbonates of Ba^{2+} and Sr^{2+} . Warming decomposes these bicarbonates into normal carbonates which are precipitated.



The solution must not be boiled otherwise insoluble carbonates with ammonium chloride are converted into soluble chlorides.



75. Can we use Na_2CO_3 in place of $(\text{NH}_4)_2\text{CO}_3$ in group V?

Ans. No. $(\text{NH}_4)_2\text{CO}_3$ is a weak electrolyte and its ionisation is suppressed by the presence of NH_4Cl . Na_2CO_3 is a strong electrolyte and in its solution $[\text{CO}_3^{2-}]$ is pretty high to precipitate even MgCO_3 in the group V.

76. Why do we test group V cations in the order of Ba, Sr and Ca?

Ans. This order is selected on the basis of the following facts:

- Only the chromate of barium is insoluble in acetic acid whereas those of calcium and strontium are soluble in acetic acid.
- Both barium and strontium form insoluble sulphates but calcium does not.
- The oxalates of barium, strontium and calcium are insoluble.

77. Why is only acetic acid employed for dissolving the group V ppt?

Ans. It is due to the following reasons:

- If H_2SO_4 is used, Ba^{2+} , Sr^{2+} and Ca^{2+} will be precipitated as their sulphates.
- If the ppt. is dissolved either in dilute HCl or in dil. HNO_3 , calcium will not be precipitated by adding $(\text{NH}_4)_2\text{C}_2\text{O}_4$ because CaC_2O_4 formed is soluble in both dil. HCl and dil. HNO_3 .

However, the use of CH_3COOH is free from the above difficulties. Hence it is used for dissolving the group V precipitates.

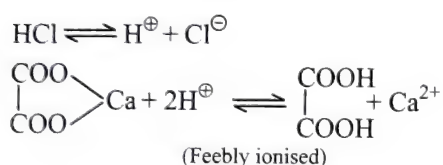
78. Sometimes no precipitate is obtained even if group V radicals are present. Why?

Ans. No, precipitate is obtained when the solution is dilute. In dilute solution, $(\text{NH}_4)_2\text{CO}_3$ hydrolyses to give carbonic acid which is a weak electrolyte. Its ionisation does not produce sufficient CO_3^{2-} ion concentration to precipitate Ca, Sr and Ba as carbonates.



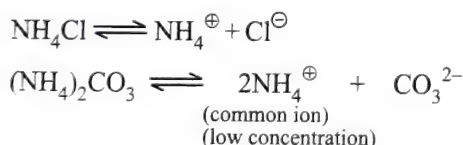
79. Calcium oxalate is soluble in dilute HCl. Explain.

Ans. When dilute HCl is added to calcium oxalate, the oxalate ions will combine with H^+ ions of HCl to give feebly ionised soluble oxalic acid.



80. Why is a precipitate of magnesium carbonate not formed along with the carbonates of Ba, Sr and Ca in group V?

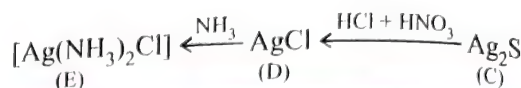
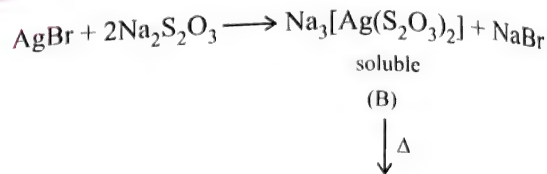
Ans. Magnesium requires higher concentration of CO_3^{2-} ions for its precipitation as MgCO_3 which is insufficient in group V due to the presence of NH_4Cl along with $(\text{NH}_4)_2\text{CO}_3$. NH_4Cl suppresses the ionisation of $(\text{NH}_4)_2\text{CO}_3$ thereby a low concentration of CO_3^{2-} ions is made available due to common ion effect.



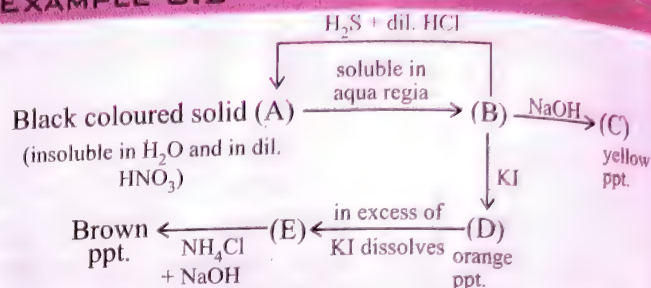
81. At times a white ppt. is obtained in group VI even in the absence of Mg. Explain.

Ans. The cations of group V which escape precipitation, now precipitate in group VI.

Sol. (A) is AgBr (present in photographic plate)

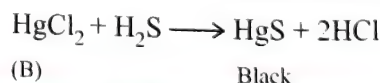
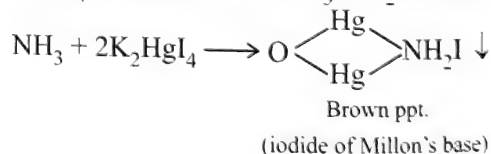
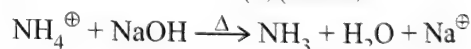
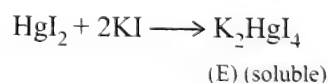
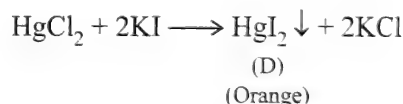
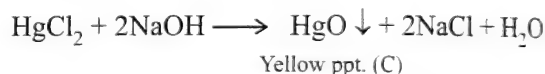
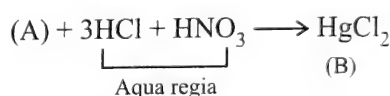


EXAMPLE 8.2



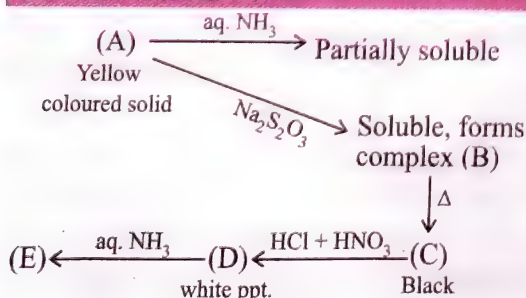
Sol. (A) is insoluble in dil. HNO_3 .

\Rightarrow (A) is of group II (copper sub-group) and is HgS
[Only HgS (black) is insoluble in dil. HNO_3]



Solved Examples

EXAMPLE 8.1



EXAMPLE 8.3

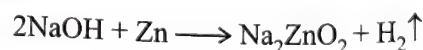
(A), an important laboratory reagent, turns red litmus blue, imparts golden yellow colour in flame and is a good precipitating agent. (A) reacts with Zn or Al forming H_2 gas. (A) gives white ppt. with ZnCl_2 or AlCl_3 but ppt. dissolves in excess of (A). What is (A) and explain reactions.

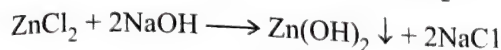
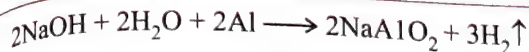
Sol. (A) turns blue litmus red \Rightarrow (A) is basic in nature.

(A) imparts golden yellow colour in flame \Rightarrow (A) has Na^+

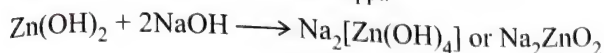
(A) gives H_2 gas with Zn or Al \Rightarrow (A) is NaOH.

Explanation:

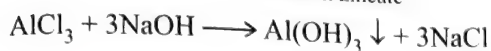




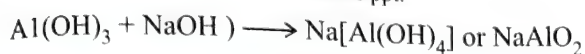
White ppt.



Sodium zincate



White ppt.

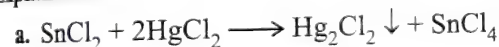


Sodium meta-aluminate

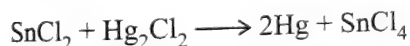
EXAMPLE 8.4

Identify (A) based on the following facts:

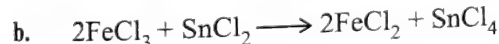
- (A) reduces HgCl_2 solution to white ppt. changing to grey.
- (A) turns FeCl_3 yellow coloured solution to green.
- (A) gives white ppt. with NaOH soluble in excess of NaOH .
- (A) gives yellow dirty ppt. on passing H_2S gas, soluble in yellow ammonium sulphide (YAS).
- (A) gives chromyl chloride test.

Sol. (A) gives yellow dirty ppt. soluble in YAS \Rightarrow (A) has Sn^{2+} (A) gives chromyl chloride test (of Cl^\ominus) \Rightarrow (A) has Cl^\ominus .(A) is SnCl_2 **Explanation:**

White

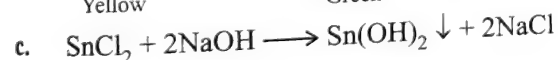


Grey

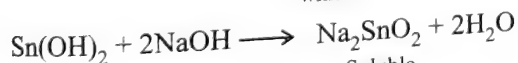


Yellow

Green

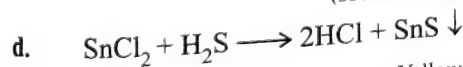


white

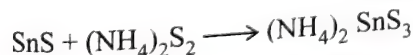


Soluble

(sodium stannite)



Yellow

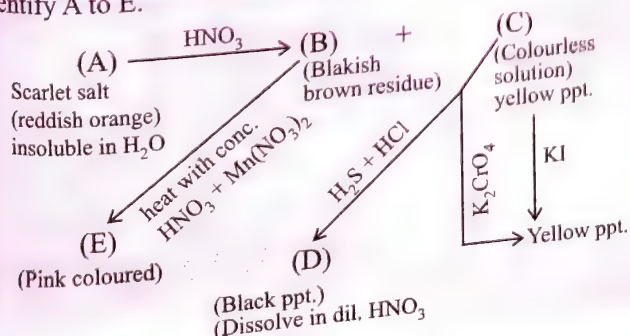


YAS

Soluble

EXAMPLE 8.5

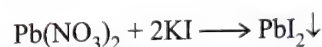
Identify A to E.

**Sol.** (C) is colourless soluble solution.(C) give black ppt. with $\text{H}_2\text{S}/\text{HCl}$ \Rightarrow (C) is of group II(C) gives yellow ppt. with KI as well as with K_2CrO_4 \Rightarrow (C) has Pb^{2+} Thus (C) is $\text{Pb(NO}_3)_2$ obtained from (A). (B) on heating with Mn^{2+} and HNO_3 gives purple colour which is due to oxidation of Mn^{2+} to HMnO_4 (purple) \Rightarrow (B) is oxidising agent \Rightarrow (B) is PbO_2 (blackish-brown) \Rightarrow (A) is double oxide of lead.(A) is Pb_3O_4 (red lead) ($2\text{PbO} \cdot \text{PbO}_2$)

(A)

(B)

(C)

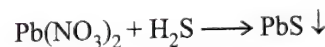


(C)

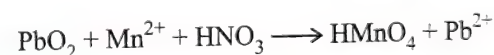
Yellow



Yellow



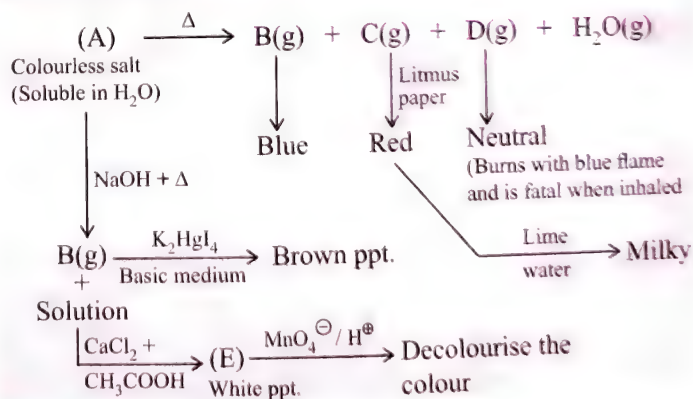
(D) black



(E) pink

EXAMPLE 8.6

Identify A to E.

**Sol.** Gas (B) gives brown ppt. with K_2HgI_4 \Rightarrow gas (B) is NH_3 \Rightarrow (A) has NH_4^+

Gas (C) turns lime water milky

 \Rightarrow gas (C) can be SO_2 or CO_2

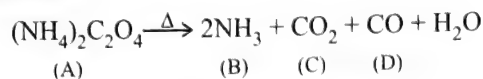
Gas (D) is also obtained along with (C). Gas (D) burns with blue flame and is fatal when inhaled

 \Rightarrow gas (D) is CO \Rightarrow gas (C) is CO_2 \Rightarrow (A) has $\text{C}_2\text{O}_4^{2-}$

It is confirmed by the fact that CaCl_2 gives white ppt.

 $\text{CaC}_2\text{O}_4 (\text{E})$ which decolourises $\text{MnO}_4^-/\text{H}^+$
$$\Rightarrow \text{(A) is } (\text{NH}_4)_2\text{C}_2\text{O}_4$$

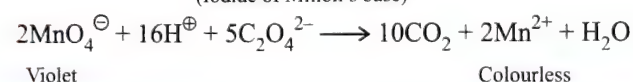
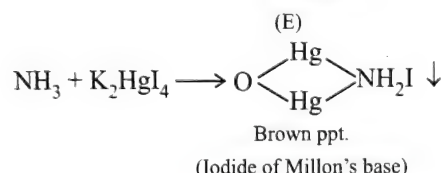
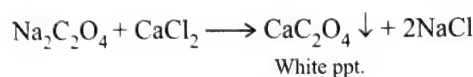
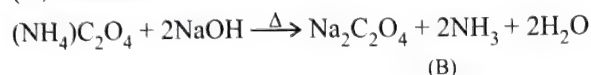
Explanation:



(B) is blue towards litmus (basic)

(C) is red towards litmus (acidic)

(D) is neutral



EXAMPLE 8.7

Name one common reagent that can precipitate or react and differentiate following pairs:

- a. Ag^{\oplus} and Ba^{2+} b. Cu^{2+} , Pb^{2+}
c. I^{\ominus} and Cl^{\ominus} d. I^{\ominus} and Br^{\ominus}
e. SO_3^{2-} and SO_4^{2-} f. Fe^{3+} , Cu^{2+}
g. Co^{2+} and Cu^{2+}

Sol.

- a. K_2CrO_4 :
- $$2Ag^{\oplus} + CrO_4^{2-} \longrightarrow Ag_2CrO_4 \downarrow$$
- Red
- $$Ba^{2+} + CrO_4^{2-} \longrightarrow BaCrO_4 \downarrow$$
- Yellow
- b. K_2CrO_4 :
- $$Cu^{2+} + CrO_4^{2-} \longrightarrow CuCrO_4 \downarrow$$
- Chocolate
- $$Pb^{2+} + CrO_4^{2-} \longrightarrow PbCrO_4 \downarrow$$
- Yellow
- c. $AgNO_3$:
- $$Ag^{\oplus} + I^{\ominus} \longrightarrow AgI \downarrow \qquad Ag^{\oplus} + Cl^{\ominus} \longrightarrow AgCl \downarrow$$
- Yellow White
- d. Cl_2 water + $CHCl_3$:
- $$2I^{\ominus} + Cl_2 \longrightarrow I_2 + 2Cl^{\ominus} \qquad 2Br^{\ominus} + Cl_2 \longrightarrow Br_2 + 2Cl^{\ominus}$$
- (Violet in (Orange in
 $CHCl_3$ layer) $CHCl_3$ layer)
- e. $BaCl_2$:
- $$BaCl_2 + SO_3^{2-} \longrightarrow BaSO_3 \downarrow$$
- White ppt. soluble in conc. HCl
- $$BaCl_2 + SO_4^{2-} \longrightarrow BaSO_4 \downarrow$$
- White ppt. insoluble in conc. HCl

- f. NH_4SCN :**
 $\text{Fe}^{3+} + \text{SCN}^- \longrightarrow [\text{Fe}(\text{SCN})]^{2+}$
 Red colour
 $\text{Cu}^{2+} + 2\text{SCN}^- \longrightarrow \text{Cu}(\text{SCN})_2 \downarrow$
 Black
- g. NH_4SCN :**
 $\text{Co}^{2+} + 4\text{SCN}^- \longrightarrow [\text{Co}(\text{SCN})_4]^{2-}$
 Blue colour
 $\text{Cu}^{2+} + 2\text{SCN}^- \longrightarrow \text{Cu}(\text{SCN})_2 \downarrow$
 Black

EXAMPLE 8.8

What single reagent solution (including H_2O) could be used to effect the separation of the following of solids?

- a. NaOH and $\text{Fe}(\text{OH})_3$ b. $\text{Ni}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$
c. Cr_2O_3 and $\text{Fe}(\text{OH})_3$ d. MnS and CoS
e. AgCl and AgI

Sol.

- H_2O can dissolve NaOH , $\text{Fe}(\text{OH})_3$ remains insoluble in water.
- NH_4OH dissolves $\text{Ni}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ is insoluble

$$\text{Ni}(\text{OH})_2 + 4\text{NH}_4\text{OH} \longrightarrow [\text{Ni}(\text{NH}_3)_4]^{2+}$$

Soluble
- Excess of NaOH can dissolve Cr_2O_3 but $\text{Fe}(\text{OH})_3$ remains insoluble.

$$\text{Cr}_2\text{O}_3 + 3\text{H}_2\text{O} \longrightarrow 2\text{Cr}(\text{OH})_3$$

$$\text{Cr}(\text{OH})_3 + \text{NaOH} \longrightarrow \text{Na}[\text{Cr}(\text{OH})_4]$$

Soluble
- Dilute HCl dissolves MnS soluble while CoS remains insoluble.

$$\text{MnS} + 2\text{HCl} \longrightarrow \text{MnCl}_2 + \text{H}_2\text{S} \uparrow$$
- Aq. NH_3 would dissolve AgCl while AgI remains insoluble

$$\text{AgCl} + 2\text{NH}_3(\text{aq.}) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$$

Soluble

EXAMPLE 8.9

A solution may contain any of the following ions: Fe^{3+} , Ni^{2+} , Cr^{3+} , Zn^{2+} , Mn^{2+} . Based on the experiment and results therein, indicate which of the ions would be present? Indicate any wrong information, if any. . . .

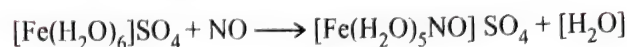
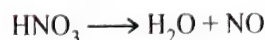
- a. The original solution is treated with $(\text{NH}_4)_2\text{S}$ (a substitute of H_2S) in a buffered basic solution. A dark precipitate is obtained.
- b. The ppt. for (a) dissolves in aqua regia.
- c. The filtrate after separating ppt. in (a) is treated with NaOH and H_2O_2 . A dark ppt. is separated. Filtrate is colourless.
- d. The ppt. from (c) dissolves in HCl (aq.) giving a coloured solution.
- e. The solution from (d) is treated with aq. NH_3 . A dark ppt. forms.
- f. The ppt. from (e) is soluble in HCl (aq.) and solution develops an intense red colour when treated with SCN^\ominus (aq.)

- Sol.**
- Precipitate can be of NiS
 - NiS dissolves in aqua regia
 - Precipitate can be of Fe(OH)₃
 - Fe(OH)₃ is soluble in HCl (aq.) giving (yellow) coloured solution of FeCl₃
 - This step is incorrect since filtrate of step (c) is already colourless indicating absence of Cr³⁺
 - This confirms Fe³⁺ by forming intense red colour

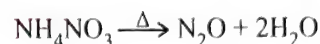
Thus, Fe³⁺ – confirmed

Ni²⁺ – probable

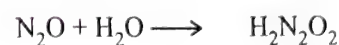
Zn²⁺, Mn²⁺, Cr³⁺ – absent



Brown coloured ring (C)

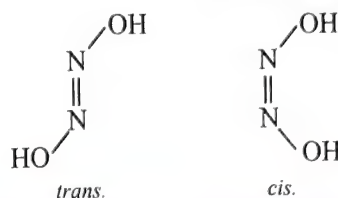


(A) (D) (E)



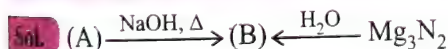
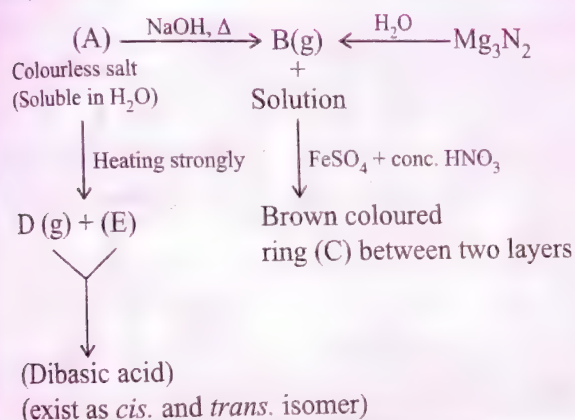
(F)

Hyponitrous acid

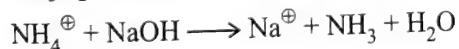
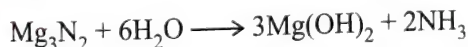


EXAMPLE 8.10

Identify A to F.

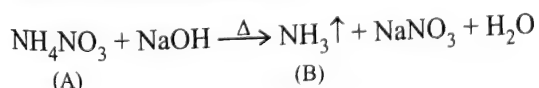


\Rightarrow N₂ has NH₄⁺ ion and (B) is NH₃



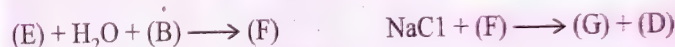
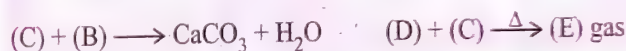
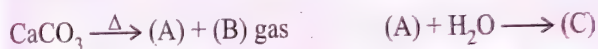
Resultant solution after NH₃ has escaped completely contains Na⁺ and anion of (A) which also gives Ring Test of NO₃⁻.

Thus, (A) is NH₄NO₃.

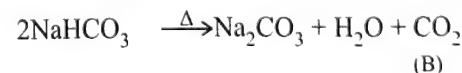
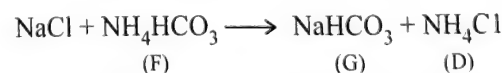
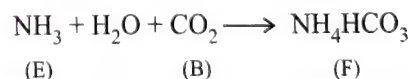
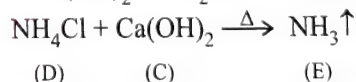
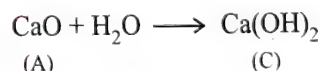
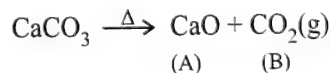


EXAMPLE 8.11

Identify (A) to (G) in the following scheme and name the process.



Sol. Scheme represents the Solvay process of manufacture of Na₂CO₃.



Exercises

Single Correct Answer Type

Part-A (Analysis of Anions)

- Which reagent is used to remove SO_4^{2-} or Cl^- from water?
 - (1) NaOH
 - (2) $\text{Pb}(\text{NO}_3)_2$
 - (3) BaSO_4
 - (4) KOH
- Which compound will **not** give positive chromyl chloride test?
 - (1) Copper chloride, CuCl_2
 - (2) Mercuric chloride, HgCl_2
 - (3) Zinc chloride, ZnCl_2
 - (4) Anilinium chloride, $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-$
- A substance on treatment with dil. H_2SO_4 liberates a colourless gas which produces (i) turbidity with baryta water and (ii) turns acidified dichromate solution green. The reaction indicates the presence of:
 - (1) CO_3^{2-}
 - (2) S^{2-}
 - (3) SO_3^{2-}
 - (4) NO_2^-
- Conc. H_2SO_4 on addition to dry KNO_3 gives brown fumes of:
 - (1) SO_2
 - (2) SO_3
 - (3) NO
 - (4) NO_2
- A white metal sulphide soluble in water is
 - (1) CuS
 - (2) Na_2S
 - (3) PbS
 - (4) ZnS
- A salt having BO_3^{3-} on burning with conc. H_2SO_4 gives edge flame.
 - (1) Green
 - (2) Yellow
 - (3) Red
 - (4) White
- KBr, on reaction with conc. H_2SO_4 , gives reddish-brown gas:
 - (1) Bromine
 - (2) Mixture of bromine and HBr
 - (3) HBr
 - (4) NO_2
- An inorganic salt when heated evolves coloured gas which bleaches moist litmus paper. The evolved gas is
 - (1) NO_2
 - (2) SO_2
 - (3) N_2O
 - (4) I_2
- The colour developed when sodium sulphide is added to sodium nitroprusside is
 - (1) Violet
 - (2) Yellow
 - (3) Red
 - (4) Black
- Using dil. HCl, which of the following radical cannot be confirmed
 - (1) S^{2-}
 - (2) $\text{S}_2\text{O}_3^{2-}$
 - (3) CO_3^{2-}
 - (4) NO_2^-
- The solution of a chemical compound X reacts with AgNO_3 solution to form a white precipitate of Y which dissolves in NH_4OH to give a complex Z. When Z is treated with dil. HNO_3 , Y reappears. The chemical compound X can be
 - (1) NaCl
 - (2) CH_3Cl
 - (3) NaBr
 - (4) NaT
- Preparation of Na_2CO_3 extract is made for acid radical analysis because:
 - (1) All anions react with Na to give water soluble compound
 - (2) Na is more reactive
 - (3) Na_2CO_3 is water soluble
 - (4) None of the above
- H_2S and SO_2 can be distinguished by
 - (1) Litmus paper
 - (2) MnO_4^-
 - (3) $\text{Pb}(\text{CH}_3\text{COO})_2$
 - (4) HCl
- Two test tubes containing a nitrate and a bromide are treated separately with H_2SO_4 brown fumes evolved are passed in water. The water will be coloured by vapours evolved from the test tube containing:
 - (1) Nitrate
 - (2) Bromide
 - (3) Both (a) and (b)
 - (4) None of these
- A solution of white crystals gives a yellow precipitate with AgNO_3 but no precipitate with a solution of Na_2CO_3 . The action of conc. H_2SO_4 on the crystals yields a brown gas. The crystals are of:
 - (1) NaNO_3
 - (2) KCl
 - (3) $\text{Ca}(\text{ON}_3)_2$
 - (4) NaBr
- A white precipitate insoluble in conc. HNO_3 is formed when aqueous solution of X in NaOH is treated with barium chloride and bromine water. The X is
 - (1) SO_3
 - (2) SO_2
 - (3) CO_2
 - (4) none of these
- Aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ on reaction with Cl_2 water gives
 - (1) $\text{Na}_2\text{S}_4\text{O}_4$
 - (2) Na_2SO_4
 - (3) $\text{Na}_2\text{S}_4\text{O}_6$
 - (4) NaOH
- When CS_2 layer containing both Br_2 and I_2 is shaken with excess of Cl_2 water, the violet colour due to I_2 disappears and a pale yellow colour appears in the solution. The disappearance of violet colour and appearance of pale yellow colour is due to the formation of:
 - (1) I_3^- and Br_2 , respectively
 - (2) HIO_3 and BrCl , respectively
 - (3) ICl and BrCl , respectively
 - (4) I^- and Br^- , respectively
- Which of the following pair of acid radicals can be distinguished by using dil. H_2SO_4 ?
 - (1) $\text{C}_2\text{O}_4^{2-}$ and NO_3^-
 - (2) NO_3^- and NO_2^-
 - (3) Cl^- and Br^-
 - (4) HCO_3^- and CO_3^{2-}
- The aqueous solution of salt gives white ppt. with lead acetate solution which is insoluble in hot water and nitric acid. The salt contains

- (1) Cl^\ominus (2) Ba^{2+}
 (3) CO_3^{2-} (4) SO_4^{2-}
21. Some pale-green crystals are strongly heated. The gases given off are passed into a container surrounded by ice and then through a solution of acidified KMnO_4 . The KMnO_4 is decolorised, a waxy white solid is formed in the ice container; this is dissolved in water. The solution will
- Give a precipitate with silver nitrate solution
 - Give a precipitate with barium chloride solution
 - Turn red litmus blue
 - Give blue colour with starch solution
22. For testing sodium carbonate solution for the presence of sulphate ions as impurities one should add:
- Excess hydrochloric acid and silver nitrate solution
 - Excess sulphuric acid and silver nitrate solution
 - Excess nitric acid and silver nitrate solution
 - Excess hydrochloric acid and barium chloride solution
23. Salt A $\xrightarrow{\text{Layer test}}$ If reddish-brown layers come first, then
- Br^\ominus present (2) Br^\ominus absent
 - Cl^\ominus present (4) I^\ominus present
24. $\text{CaCO}_3(\text{s}) + \text{CH}_3\text{COOH} \xrightarrow{\text{Na}_2\text{C}_2\text{O}_4 \text{ solution}} ?$
 Comment on the product of this reaction.
- No reaction
 - White ppt. of $(\text{CH}_3\text{COO})_2\text{Ca}$ is obtained
 - White ppt. of CaC_2O_4 is formed
 - No ppt. is obtained

Part-B (Dry Tests)

25. The compound formed in the borax bead test of Cu^{2+} ion in oxidising flame is
- Cu (2) CuBO_2
 - $\text{Cu}(\text{BO}_2)_2$ (4) none of these
26. Potassium chromate solution is added to an aqueous solution of a metal chloride. The precipitates thus obtained are insoluble in acetic acid. These are subjected to flame test; the colour of the flame is
- Lilac (2) Apple green
 - Crimson red (4) Golden yellow
27. Which cation is detected by the flame test?
- NH_4^\oplus (2) K^\oplus
 - Mg^{2+} (4) Al^{3+}
28. Which gives violet colour with borax?
- Fe (2) Pb
 - Co (4) Mn
29. A green mass is formed in the charcoal cavity test when a colourless salt (X) is fused with cobalt nitrate. (X) may contain
- Aluminium (2) Copper
 - Barium (4) Zinc

30. Carbonates of Ba, Sr and Ca are

- White (2) Blue
 - Green (4) Yellow
31. The metal that does not give the borax bead test is
- Cr (2) Ni
 - Pb (4) Mn
32. Which metal gives blue ash when its salt is heated with Na_2CO_3 solid and $\text{Co}(\text{NO}_3)_2$ on a charcoal piece?
- Cu (2) Mg
 - Al (4) Zn
33. A minute quantity of cupric salt is heated on borax bead in reducing flame of Bunsen burner; the colour of bead after cooling will be
- Blue (2) Red
 - Colourless (4) Green
34. Aqueous solution of a salt (Y) is alkaline to litmus. On strong heating, it swells-up to give a glassy material. When conc. H_2SO_4 is added to a hot concentrated solution of (Y), white crystals of a weak acid separate out. Hence, the compound (Y) is
- $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (2) $\text{Ca}_2\text{P}_6\text{O}_{11} \cdot 10\text{H}_2\text{O}$
 - $\text{Na}_2\text{B}_6\text{O}_{11}$ (4) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

Part-C (Analysis of Cations)

35. Strongly acidified solution of barium nitrate gives a white precipitate with which did not dissolve even after large addition of water.
- Sodium phosphate (2) Sodium carbonate
 - Sodium sulphate (4) Sodium chloride
36. In the precipitation of the iron group in qualitative analysis, ammonium chloride is added before adding ammonium hydroxide to:
- Decrease concentration of OH^\ominus ions
 - Prevent interference by phosphate ions
 - Increase concentration of Cl^\ominus ions
 - Increase concentration of NH_4^\oplus ions
37. H_2S gas, on passing through an alkaline solution, forms a white precipitate. The solution contains ions of
- Pb (2) Zn
 - Cu (4) Ni
38. Yellow ammonium sulphide solution is a suitable reagent used for the separation of
- HgS and PbS (2) PbS and Bi_2S_3
 - Bi_2S_3 and CuS (4) CdS and As_2S_3
39. An orange red precipitate obtained by passing H_2S through an acidified solution of an inorganic salt indicates the presence of
- Cadmium (2) Tin
 - Antimony (4) Bismuth
40. Excess of concentrated sodium hydroxide can separate mixture of

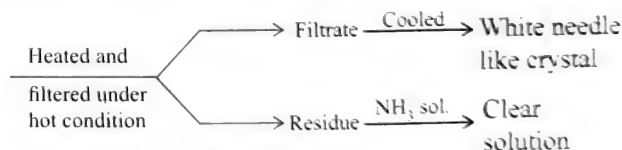
- (1) Al^{3+} and Cr^{3+} (2) Cr^{3+} and Fe^{3+}
 (3) Al^{3+} and Zn^{2+} (4) Zn^{2+} and Pb^{2+}
41. Which of the following sulphides has the maximum solubility product?
 (1) HgS (2) PbS
 (3) CuS (4) MnS
42. Lead has been placed in qualitative group analysis 1st and 2nd because:
 (1) It shows the valency one and two
 (2) It forms insoluble PbCl_2
 (3) It forms lead sulphide
 (4) PbCl_2 is partially soluble in water
43. As_2S_3 is
 (1) Black (2) Yellow
 (3) Orange (4) White
44. A black sulphide is formed by the action of H_2S on
 (1) CuCl_2 (2) CdCl_2
 (3) ZnCl_2 (4) NaCl
45. The group II precipitates soluble in yellow ammonium sulphide may be
 (1) As, Sb, Sn (2) Cu, Hg, Bi, Cd
 (3) Both (a) and (b) (4) None of these
46. Nitric acid is generally not used for preparation of original solution in analysis of basic radicals, because it
 (1) is oxidising agent (2) is reducing agent
 (3) forms insoluble nitrates (4) forms soluble nitrates
47. The sulphide not soluble in hot dilute nitric acid is
 (1) CuS (2) ZnS
 (3) CdS (4) HgS
48. H_2S will precipitate the sulphides of all the metals from the solution of chlorides of Cu, Zn and Cd if
 (1) The solution is aqueous
 (2) The solution is acidic
 (3) The solution is dilute acidic
 (4) Any of the above solutions is present
49. To a solution of a substance, gradual addition of ammonium hydroxide results in a black precipitate which does not dissolve in excess of NH_4OH . However, when HCl is added to the original solution, a white precipitate is formed. The solution contained
 (1) Lead salt (2) Silver salt
 (3) Mercurous salt (4) Copper salt
50. A compound is soluble in water. If ammonia is added to aqueous solution of the compound, a brown precipitate appears which is soluble in dil. HCl . The compound has
 (1) Aluminium (2) Zinc
 (3) Iron (4) Cadmium
51. A light green coloured salt soluble in water gives black precipitate on passing H_2S which dissolves readily in HCl . The metal ion present is
 (1) Co^{2+} (2) Fe^{2+}
 (3) Ni^{2+} (4) Ag^{\oplus}
52. All ammonium salts liberate ammonia when:
 (1) Heated with HCl (2) Heated with caustic soda
 (3) Heated with H_2SO_4 (4) Heated with NaNO_2
53. Manganese salt + PbO_2 + conc. $\text{HNO}_3 \longrightarrow$ The solution has purple colour.
 The colour is due to
 (1) HMnO_4 (2) A lead salt
 (3) $\text{Mn}(\text{NO}_3)_2$ (4) H_2MnO_4
54. An orange precipitate of group II is dissolved in conc. HCl ; the solution when treated with excess of water turns milky due to formation of
 (1) $\text{Sn}(\text{OH})\text{Cl}$ (2) $\text{Sb}(\text{OH})\text{Cl}_2$
 (3) SbOCl (4) $\text{Sb}(\text{OH})_2\text{Cl}$
55. Which of the following solutions gives precipitate with $\text{Pb}(\text{NO}_3)_2$ but not with $\text{Ba}(\text{NO}_3)_2$?
 (1) Sodium chloride (2) Sodium sulphate
 (3) Sodium nitrate (4) Sodium hydrogen phosphate
56. A white powder when strongly heated gives off brown fumes. A solution of this powder gives a yellow precipitate with a solution of KI . When a solution of barium chloride is added to a solution of powder, a white precipitate results.
 This white powder may be
 (1) A soluble sulphate (2) KBr or NaBr
 (3) $\text{Ba}(\text{NO}_3)_2$ (4) AgNO_3
57. The ion that **cannot** be precipitated by both by HCl and H_2S is
 (1) Pb^{2+} (2) Cu^{\oplus}
 (3) Ag^{\oplus} (4) Sn^{2+}
58. The presence of magnesium is confirmed in the qualitative analysis by the formation of a white crystalline precipitate of:
 (1) $\text{Mg}(\text{HCO}_3)_2$ (2) MgNH_4PO_4
 (3) $\text{MgNH}_4(\text{HCO}_3)_3$ (4) MgCO_3
59. In qualitative inorganic analysis, phosphate, if present, is to be eliminated in the appropriate group in order to detect the radical:
 (1) Pb^{2+} (2) As^{3+}
 (3) Ca^{2+} (4) Cd^{2+}
60. Na_2CO_3 cannot be used in place of $(\text{NH}_4)_2\text{CO}_3$ for the precipitation of group V because
 (1) Na^{\oplus} interferes in the detection of group V
 (2) Concentration of CO_3^{2-} is very low
 (3) Na will react with acid radicals
 (4) Mg will be precipitated
61. Disodium hydrogen phosphate is used to test:
 (1) Mg^{2+} (2) Na^{\oplus}
 (3) Ca^{2+} (4) All of these
62. Reddish-brown (chocolate) ppt. is formed with:

- (1) Cu^{2+} and $\text{Fe}(\text{CN})_6^{4-}$ (2) Ba^{2+} and SO_4^{2-}
 (3) Pb^{2+} and I^- (4) None of these
63. Addition of SnCl_2 to HgCl_2 gives ppt.:
- (1) White turning to grey (2) Black turning to white
 (3) White turning to red (4) None of these
64. To avoid the precipitation of hydroxides of Ni^{2+} , Co^{2+} , Zn^{2+} and Mn^{2+} along with those of Fe^{3+} , Al^{3+} and Cr^{3+} the third group solution should be
- (1) Heated with a few drops of conc. HNO_3
 (2) Treated with excess of NH_4Cl
 (3) Concentrated
 (4) None of these
65. Which gives a white precipitate with a solution of AgNO_3 , a white precipitate with dil. H_2SO_4 , and a green flame test?
- (1) Copper chloride (2) Copper nitrate
 (3) Lead nitrate (4) Barium chloride
66. In qualitative inorganic analysis of basic radicals, hydrochloric acid is preferred to nitric acid for preparing a solution of given substance. This is because:
- (1) Nitrates are not decomposed to sulphides
 (2) Nitric acid contains nitrogen
 (3) Hydrochloric acid is not an oxidising agent
 (4) Chlorides are easily converted to sulphides
67. Addition of solution of oxalate to an aqueous solution of mixture of Ba^{2+} , Sr^{2+} and Ca^{2+} will precipitate:
- (1) Ca^{2+} (2) Ca^{2+} and Sr^{2+}
 (3) Ba^{2+} and Sr^{2+} (4) All the three
68. The reagent that distinguishes between silver and lead salt is
- (1) H_2S gas
 (2) dil. HCl solution added after this dissolved in hot water
 (3) NH_4Cl (solid) + NH_4OH (solution)
 (4) NH_4Cl (solid) + $(\text{NH}_4)_2\text{CO}_3$ solution
69. Sulphide ions react with $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5]$ to form a purple coloured compound $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$. In the reaction, the oxidation state of iron;
- (1) Changes from +2 to +3 (2) Changes from +3 to +2
 (3) Changes from +2 to +4 (4) Does not change
70. The product of reaction of an aq. solution of Bi^{3+} salt with sodium thiosulphate gives:
- (1) BiS (2) $\text{Bi}_2(\text{S}_2\text{O}_3)_3$
 (3) $\text{Na}[\text{Bi}(\text{S}_2\text{O}_3)_2]$ (4) $[\text{Bi}_2(\text{S}_2\text{O}_3)_2]\text{Cl}_2$
71. $(\text{A}) + \text{HClO}_4 \longrightarrow \text{B} + \text{C} \text{ (Filtrate)}$
 (Mix. of two cation) White ppt. $\downarrow \text{NaOH}$
 Brown ppt. $\longleftarrow \text{K}_2\text{HgI}_4/\text{OH}^-$ D
- The cations present in A are
- (1) K^+ and Na^+ (2) K^+ and NH_4^+
 (3) NH_4^+ and Fe^{2+} (4) Mg^{2+} and Na^+
72. Few drops of HNO_3 are added to group II before proceeding to group III in order to:

- (1) Convert Fe^{2+} to Fe^{3+} (2) Convert Fe^{3+} to Fe^{2+}
 (3) ppt. group III (4) None of these
73. A reddish-pink substance on heating gives off a vapour which condenses on the sides of the test tube and the substance turns blue. If on cooling water is added to the residue, it turns to its original colour. The substance is
- (1) Iodine crystals (2) Copper sulphate crystals
 (3) Cobalt chloride crystals (4) Zinc oxide
74. An inorganic Lewis acid (X) fumes in moist air, and intensity of fumes increases when a rod dipped in NH_4OH is brought near to it. An acidic solution of (X) on addition of NH_4Cl and NH_4OH gives a precipitate which dissolves in NaOH solution. An acidic solution of (X) does not give precipitate with H_2S . Hence, the compound (X) is
- (1) FeCl_3 (2) AlCl_3
 (3) SnCl_2 (4) ZnCl_2
75. A colourless salt (X) is soluble in water and also in alcohol and amines. On strong heating, (X) gives a brown gas (Y) and a grey residue. (X) dissolves in ammonia to give a solution (Z) which gives silver mirror with aldehydes. A solution of (X) is easily reduced by iron (II) sulphate. A solution of (X) also gives a brick red precipitate with potassium dichromate solution. Hence, choose the correct alternative:

	X	Y	Z
(1)	$\text{Pb}(\text{NO}_3)_2$	NO_2	Ag_2O
(2)	AgNO_3	NO	$[\text{Ag}(\text{NH}_3)_2]^+$
(3)	AgNO_3	NO_2	Ag_2O
(4)	AgNO_3	NO_2	$[\text{Ag}(\text{NH}_3)_2]^+$

76. Salt mixture $\xrightarrow{\text{dil. HCl}}$ White ppt.



Salt is consisting of cations:

- (1) Pb^{2+} and Hg^{2+} (2) Pb^{2+} and Hg_2^{2+}
 (3) Pb^{2+} and Ag^+ (4) Pb^{2+} , Hg_2^{2+} and Ag^+
77. $\text{Hg}(\text{NO}_3)_2 \xrightarrow{\Delta} \text{W} + \text{X} + \text{O}_2$
 $\text{X} + \text{H}_2\text{O} \longrightarrow \text{HNO}_2 + \text{HNO}_3$
 $\text{W} + \text{HNO}_3 \longrightarrow \text{Y} + \text{NO} + \text{H}_2\text{O}$
 $\text{Y} + \text{Na}_2\text{S}_2\text{O}_3(\text{excess}) \longrightarrow \text{Z} + \text{NaNO}_3$
- | W | X | Y | Z |
|--------------------|--------------------------|----------------------------|--------------------------------------------------|
| (1) Hg , | N_2O , | $\text{Hg}(\text{NO}_3)_2$ | $\text{Na}_2[\text{Hg}(\text{S}_2\text{O}_3)_2]$ |
| (2) HgO , | NO , | $\text{Hg}(\text{NO}_3)_2$ | $\text{Na}[\text{Hg}(\text{S}_2\text{O}_3)_2]$ |
| (3) Hg , | NO_2 , | $\text{Hg}(\text{NO}_3)_2$ | $\text{Na}_2[\text{Hg}(\text{S}_2\text{O}_3)_2]$ |
| (4) Hg , | N_2O_4 , | $\text{Hg}(\text{NO}_3)_2$ | $\text{Na}_3[\text{Hg}(\text{S}_2\text{O}_3)_2]$ |

Part-D (Miscellaneous)

78. Prussian blue is formed when:

- (1) Ferrous sulphate reacts with FeCl_3
 (2) Ferric sulphate reacts with $\text{K}_4[\text{Fe}(\text{CN})_6]$

- (3) Ferrous ammonium sulphate reacts with FeCl_3
 (4) Ammonium sulphate reacts with FeCl_3
79. A metal salt solution forms a yellow precipitate with potassium chromate in acetic acid, a white precipitate with dil. sulphuric acid, but gives no precipitate with sodium chloride or iodide. The white precipitate obtained when sodium carbonate is added to the metal salt solution consists of
 (1) Lead carbonate (2) Basic lead carbonate
 (3) Barium carbonate (4) Strontium carbonate
80. Chemical volcano is produced on heating:
 (1) $\text{K}_2\text{Cr}_2\text{O}_7$ (2) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
 (3) ZnCr_2O_7 (4) K_2CrO_4
81. $\text{A} \xrightarrow{\Delta} \text{B} + \text{C}_{(\text{g})} + \text{D}_{(\text{g})}$
 (Solid) Brown residue
 \downarrow Aqueous NaOH
 E (dirty green precipitate) $\xrightarrow[\text{to air}]{\text{On exposure}}$ F
 Identify A.
 (1) FeCl_3 (2) $\text{Fe}_2(\text{SO}_4)_3$
 (3) FeSO_4 (4) All are correct
82. $(\text{D}) \xleftarrow[\text{presence of HCl}]{\text{BaCl}_2 \text{ in}}$ (A) $\xrightarrow[\text{with } \text{K}_2\text{HgI}_4]{\text{aq. solution}}$ (B)
 White ppt. (Light green) crystalline compound Brown ppt.
 \downarrow Aqueous solution with $\text{K}_3[\text{Fe}(\text{CN})_6]$
 (C) Blue
 Identify A.
 (1) FeSO_4 (2) $(\text{NH}_4)_2\text{SO}_4$
 (3) $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (4) All are correct
83. $\text{Fe} + \text{conc. HNO}_3 \longrightarrow \text{X}$. Then X will be ($> 80\%$)
 (1) Fe_2O_3 (2) FeO
 (3) Fe_3O_4 (4) None of these
84. Yellow coloured solution of FeCl_3 changes to light green when:
 (1) SnCl_2 is added (2) Zn is added
 (3) H_2S gas is passed (4) All true
85. Fe^{2+} does not give blue colour with $\text{K}_4[\text{Fe}(\text{CN})_6]$ but on its reaction with (X), blue colour appears. (X) can be:
 (1) $\text{MnO}_4^- / \text{H}^+$ (2) H_2SO_4
 (3) NH_3 (4) HCl
86. $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ ppt. are separated by
 (1) Aq. NH_3 (2) HCl
 (3) $\text{NaOH} / \text{H}_2\text{O}_2$ (4) H_2SO_4
87. Turnbull's blue and Prussian's blue respectively are
 $\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]^{2-}$ (I) $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ (II)
 $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^\ominus$ (III) $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^\ominus$ (IV)
- (1) I, II (2) I, III
 (3) III, IV (4) IV, III
88. Which of the following are soluble in excess of NaOH
 (X): As_2S_3 (Y): CuS ; (Z): AlCl_3 ;
 (1) X, Y, Z (2) Y, Z
 (3) X, Z (4) X, Y
89. A mixture on heating gave a gas used as an anaesthetic, soluble in water forming cis., and trans. dibasic acid. 1.1 g of gas occupies 0.56 L at STP. Mixture contains
 (1) $\text{NaNO}_3 + \text{NH}_4\text{Cl}$ (2) $\text{NaNO}_2 + \text{NH}_4\text{Cl}$
 (3) $\text{CaCO}_3 + \text{MgCO}_3$ (4) $\text{NH}_4\text{Cl} + \text{Na}_2\text{SO}_4$
90. Aq. solution contains $\text{Zn}(\text{CH}_3\text{COO})_2$, $\text{Cd}(\text{CH}_3\text{COO})_2$ and $\text{Cu}(\text{CH}_3\text{COO})_2$. On passing H_2S gas, there is precipitation of as sulphide:
 (1) Zn^{2+} , Cd^{2+} (2) Cu^{2+} , Cd^{2+}
 (3) Zn^{2+} , Cu^{2+} (4) Zn^{2+} , Cu^{2+} , Cd^{2+}
91. Ferric alum gives red colour with NH_4SCN due to formation of
 (1) $\text{Al}(\text{SCN})_3$ (2) $[\text{Fe}(\text{SCN})_3]^\ominus$
 (3) $\text{Fe}(\text{SCN})_3$ (4) $[\text{Fe}(\text{SCN})]^{2+}$
92. Colourless salt (X) $\xrightarrow{\Delta}$ (Y) $\xrightarrow[\text{coloured bead (Z)}]{\text{Cu}^{2+}, \Delta}$
 (X) can be
 (1) borax (2) micro-cosmic salt
 (3) both (4) none
93. $\text{KCl} + \text{conc. H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} (\text{X}) \xrightarrow[\text{(Y)}]{\text{NaOH}}$
 (X) is reddish brown coloured gas soluble in NaOH forming (Y). (X) and (Y) are
 (1) Cr_2OCl_2 , Na_2CrO_3 (2) $\text{Cr}_2\text{O}_2\text{Cl}_2$, Na_2CrO_3
 (3) CrO_2Cl , Na_2CrO_4 (4) CrO_2Cl_2 , Na_2CrO_4
94. Aqueous solution of BaBr_2 gives yellow ppt. with
 (1) K_2CrO_4 (2) AgNO_3
 (3) both (4) none
95. $\text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons[\text{pH} = y]{\text{pH} = x} \text{CrO}_4^{2-}$
 orange green
 This change is based on change in pH. Probable values of x and y can be
 (1) 8, 6
 (2) 8, 10
 (3) 4, 6
 (4) change is independent of pH
96. H_2S would separate the following in $\text{pH} < 7$:
 (1) Zn^{2+} , Co^{2+} (2) Cu^{2+} , Cd^{2+}
 (3) Cu^{2+} , Cr^{3+} (4) Cu^{2+} , As^{3+}
97. Solution of (X) in dil. $\text{HCl} + \text{H}_2\text{O} \longrightarrow$ white turbidity. (X) $\xrightarrow{\text{H}_2\text{S}/\text{HCl}}$ black ppt. (Y). (Y) is soluble in
 (1) NaOH (2) YAS
 (3) HNO_3 (4) HCl

98. $K_2Cr_2O_7 + \text{conc. } H_2SO_4 + H_2O_2 + \text{ether} \longrightarrow \text{blue}$
perchromic anhydride (in ethereal layer). Blue colour is due to

- (1) CrO_3 (2) H_2CrO_4
(3) $H_2Cr_2O_3$ (4) CrO_5

99. There is foul smell in presence of moisture with

- (1) $AlCl_3$ (2) $Al_2(SO_4)_3$
(3) FeS (4) $FeSO_4$

100. $AgNO_3$ gives white ppt. with hypo changing to black after some time. Black ppt. is of

- (1) $Ag_2S_2O_3$ (2) Ag_2SO_4
(3) $Ag_2S_4O_6$ (4) Ag_2S

101. SO_2 and CO_2 both turn lime water (A) milky, SO_2 also turns $K_2Cr_2O_7/H^+$ (B) green while O_2 is soluble in pyrogallol (C) turning it black. These gases are to be detected in order by using these reagents. The order is

- (1) (A), (B), (C) (2) (B), (C), (A)
(3) (B), (A), (C) (4) (A), (C), (B)

102. Aluminium sulphate (X) is slightly insoluble in water. It is converted into soluble sodium sulphate by using Na_2CO_3 in the preparation of sodium carbonate extract. Mole of Na_2CO_3 , required for complete conversion of 1 mole of (X) into soluble sulphate, is

- (1) 1 (2) 2
(3) 3 (4) 4

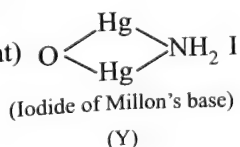
103. $CoCl_2$ gives blue colour with NH_4SCN due to formation of

- (1) $(NH_4)_2[Co(SCN)_4]$ (2) $(NH_4)_4[Co(SCN)_6]$
(3) $(NH_4)_3[Co(SCN)_6]$ (4) $(NH_4)(Co(SCN)_4]$

104. $HgCl_2 + \text{excess of } KI \longrightarrow (A) \xrightarrow{NH_3} (B).$

(A) and (B) respectively are

- (1) K_2HgI_4 (Nessler's reagent) (X)
(2) (Y) , (X)
(3) both (X)
(4) both (Y)



105. NH_4SCN can be used to test one or more out of Fe^{3+} , Co^{2+} , Cu^{2+}

- (1) Fe^{3+} only (2) Co^{2+} , Cu^{2+}
(3) Fe^{3+} , Cu^{2+} (4) all

106. $K_4[Fe(CN)_6]$ can be used to detect one or more out of Fe^{2+} , Fe^{3+} , Zn^{2+} , Cu^{2+} , Cd^{2+}

- (1) Fe^{2+} , Fe^{3+} (2) Fe^{3+} , Zn^{2+} , Cu^{2+}
(3) all but Fe^{3+} (4) all but Fe^{2+}

107. Aqueous solution of borax reacts with two mol. of acids. This is because of

- (1) formation of 2 mol. of $B(OH)_3$ only
(2) formation of 2 mol. of $[B(OH)_4]^-$ only

(3) formation of 1 mol. each of $B(OH)_3$ and $[B(OH)_4]^-$

(4) formation of 2 mol. each of $[B(OH)_4]^-$ and $B(OH)_3$, of which only $[B(OH)_4]^-$ reacts with acid

108. Ag_2S is soluble in $NaCN$ due to formation of

- (1) $Na[Ag(CN)_2]$ (2) $Ag(CN)_2$
(3) $Na_2[Ag(CN)_3]$ (4) $Na_2[Ag(CN)_2]$

109. A compound gives violet flame test and gives a white ppt. With $AgNO_3$. The compound is

- (1) $NaCl$ (2) KCl
(3) $BaCl_2$ (4) $CaCl_2$

110. Bromine vapours turns paper blue.

- (1) Starch iodide (2) Starch
(3) Lead acetate (4) Methyl orange

111. Solution of a salt in sulphanilic acid and α -naphthylamine give red ppt., due to

- (1) Br^- (2) I^-
(3) NO_2^- (4) NO_3^-

112. Solution of a salt in dil. H_2SO_4 produces deep blue colour with starch iodide solution. The salt contains

- (1) Br^- (2) I^-
(3) NO_2^- (4) NO_3^-

113. The gas which turns mercurous nitrate paper black is

- (1) NH_3 (2) Cl_2
(3) SO_2 (4) SO_3

114. A mixture when heated with dil. H_2SO_4 does not evolve brown vapours but with conc. H_2SO_4 brown vapours are obtained. The vapours when brought in contact with $AgNO_3$ soln. do not give any precipitate. The mixture contains.

- (1) NO_2^- (2) NO_3^-
(3) I^- (4) Br^-

115. To solution of a salt in acid medium, $AgNO_3$ is added, a white ppts. rapidly changing to yellow orange, brown and finally black is obtained. This is due to the presence of

- (1) SO_3^{2-} (2) $S_2O_3^{2-}$
(3) CH_3COO^- (4) S_2^-

116. Nitrite and nitrate both respond to ring test. Nitrites are removed by treating with

- (1) Conc. HNO_3 (2) NH_4Cl
(3) Conc H_2SO_4 (4) MnO_2

117. Which of the following metal oxides is white in colour but becomes yellow on heating

- (1) AgO (2) ZnO
(3) Ag_2O (4) FeO

118. Chromyl chloride test is performed for the detection of Cl^- . A salt solution containing Cl^- ion is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 , orange red vapours of CrO_2Cl_2 are obtained. On passing these vapours through a soln. of $NaOH$, a yellow ppt. due to Na_2CrO_4 is obtained. If these

- vapours are dissolved in H_2O and acetic acid and lead acetate solution is added then
- (1) The solution will remain colourless
 - (2) The solution will become dark green
 - (3) The solution will become brown
 - (4) A yellow ppt. will be obtained
119. The chromyl chloride test responds poorly with the chlorides of Pb, Ag, Sb and Sn; but fails with the chlorides of
- (1) Hg (2) As
 - (3) Bi (4) Cu
120. When a salt is heated with dil. H_2SO_4 and KMnO_4 soln., the pink colour of KMnO_4 is discharged, the mixture may contain
- (1) Sulphite (2) Carbonate
 - (3) Nitrate (4) Bicarbonate
121. Ring test for nitrates is confirmed by acidifying the soda extract of a salt solution and then adding freshly prepared FeSO_4 soln. a brown ring is formed due to the formation of $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$. This test should not be performed for nitrate ion in presence of
- (1) NO_2^- (2) Br^-
 - (3) I^- (4) All
122. Soda extract of a salt solution is acidified with excess of dil. CH_3COOH and CaCl_2 soln. is added. A white ppt. insoluble in CH_3COOH confirms.
- (1) $\text{C}_2\text{O}_4^{2-}$ (2) CO_3^{2-}
 - (3) HCO_3^- (4) $\text{S}_2\text{O}_3^{2-}$
123. When Cl_2 water is added to an excess soln. of KI in presence of CHCl_3 , a violet colour is obtained. On adding more of water, the violet colour disappears and a colourless solution is obtained. The test confirms the presence of
- (1) I^- (2) Br^-
 - (3) Cl^- (4) I^- and Br^-
124. The first group reagent is dil. HCl , which of the following **do not** belong to group I?
- (1) Ag^+ (2) Pb^{2+}
 - (3) Hg_2^{2+} (4) Hg^{2+}
125. Which of the following is not precipitated by H_2S in presence of NH_3
- (1) Co^{2+} (2) Mn^{2+}
 - (3) Fe^{3+} (4) Cd^{2+}
126. A white ppt. obtained in the analysis of a mixture becomes black on treatment with NH_4OH . It may be
- (1) Hg_2Cl_2 (2) HgCl_2
 - (3) PbCl_2 (4) AgCl
127. When excess of SnCl_2 is added to a soln. of HgCl_2 , a white ppt. turning grey is obtained the grey colour is due to the formation of
- (1) Hg_2Cl_2 (2) SnCl_4
 - (3) Sn (4) Hg
128. A white ppt. obtained in the analysis of a mixture becomes black on treatment with NH_3 or NH_4OH due to the formation of finely divided Hg and $\text{Hg}(\text{NH}_2)\text{Cl}$. The salt may be
- (1) PbCl_2 (2) AgCl
 - (3) HgCl_2 (4) Hg_2Cl_2
129. Which of the following ions will give a colourless aqueous solution
- (1) Ni^{2+} (2) Cu^+
 - (3) Cu^{2+} (4) Fe^{2+}
130. Which of the following is insoluble in dil. HNO_3
- (1) HgS (2) PbS
 - (3) Bi_2S_3 (4) CuS
131. Which of the following sulphate is insoluble in H_2O
- (1) CuSO_4 (2) PbSO_4
 - (3) CdSO_4 (4) $\text{Bi}_2(\text{SO}_4)_3$
132. Which one has the minimum solubility product?
- (1) AgCl (2) AlCl_3
 - (3) BaCl_2 (4) NH_4Cl
133. When H_2S is passed through an ammoniacal salt solution X, a white ppt. is obtained. The X can be a
- (1) Cobalt salt (2) Zinc salt
 - (3) Nickel salt (4) Manganese salt
134. With Cu^{2+} ions $[\text{Fe}(\text{CN})_6]^{4-}$ gives a ppt. of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ (Cupric ferro cyanide)
- (1) Blue (2) Green
 - (3) Chocolate (4) White
135. With Co^{+2} ions $[\text{Fe}(\text{CN})_6]^{3-}$ gives a ppt. of $\text{Co}_3[\text{Fe}(\text{CN})_6]$.
- (1) Blue (2) Reddish brown
 - (3) Chocolate (4) Green
136. With Co^{+2} ions NH_4SCN gives ppt. of $(\text{NH}_4)_2[\text{Co}(\text{CNS})_4]$ which is soluble in acetone.
- (1) Blue (2) Green
 - (3) Chocolate (4) Reddish brown
137. Pb has been placed in groups I and II because
- (1) It shows the valency of one and two
 - (2) It is partly soluble in H_2O
 - (3) It forms insoluble PbCl_2
 - (4) It forms lead sulphide
138. With Fe^{3+} ions $[\text{Fe}(\text{CN})_6]^{4-}$ gives Prussian blue colouration due to the formation of ferri-ferro cyanide, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ while with NH_4SCN , Fe^{3+} ion gives colouration
- (1) Deep red (2) Blue
 - (3) Brown (4) Green
139. A metal chloride on heating with $\text{K}_2\text{Cr}_2\text{O}_7$ gives a yellow ppt. insoluble in acetic acid. The metal may be
- (1) Hg (2) Zn
 - (3) Pb (4) Ag

140. With Zn^{2+} ions $[\text{Fe}(\text{CN})_6]^{4-}$ ions gives ppt.
 (1) Blue (2) Chocolate
 (3) Reddish brown (4) Bluish white
141. Which one among the following pairs of ions cannot be separated by H_2S in dilute HCl ?
 (1) Al^{3+} , Hg^{2+} (2) Zn^{2+} , Cu^{2+}
 (3) Bi^{3+} , Sn^{4+} (4) Ni^{2+} , Cu^{2+}
142. Which of the following pairs of ions would be expected to form precipitate when dilute solutions are mixed?
 (1) Fe^{3+} , PO_4^{3-} (2) NH_4^+ , CO_3^{2-}
 (3) Na^+ , SO_4^{4-} (4) Na^+ , S_2^{2-}
143. Which one of the following can be used in place of NH_4Cl for identification of the third group radicals?
 (1) NaCl (2) $(\text{NH}_4)_2\text{SO}_4$
 (3) $(\text{NH}_4)_2\text{CO}_3$ (4) NH_4NO_3
144. Conc. HNO_3 is added before proceeding to test for group III. This is to
 (1) Convert Fe^{+2} ion into Fe^{+3} ion
 (2) Oxidise any remaining H_2S
 (3) Form nitrates which give granular precipitates
 (4) Increase ionisation of NH_4OH
145. In IVth group, the ppt. of $\text{Mn}(\text{OH})_2$ in excess of NaOH , turns brown or black in air due to the formation of
 (1) $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ (2) MnO_2
 (3) $\text{MnO}_2 \cdot \text{H}_2\text{O}$ (4) All
146. Mg is not precipitated in group V because
 (1) MgCO_3 is soluble in H_2O
 (2) MgCO_3 is soluble in NH_4Cl
 (3) MgCO_3 is soluble in NH_4OH
 (4) All
147. In group V, $(\text{NH}_4)_2\text{CO}_3$ is added to precipitate out the carbonate, Na_2CO_3 is not added because
 (1) CaCO_3 is soluble in Na_2CO_3
 (2) MgCO_3 will be ppt. out in group V
 (3) Na_2CO_3 increase the solubility of group V carbonates
 (4) All
148. DMG gives a rosy red crystalline ppt. with
 (1) Zn^{2+} (2) Ni^{2+}
 (3) Co^{2+} (4) Mn^{2+}
149. H_2S in the presence of HCl precipitates group II radicals but not of group IV because
 (1) HCl activates H_2S .
 (2) HCl increases conc. of Cl^- due to common ion effect.
 (3) HCl decreases conc. of S^{2-} due to common ion effect.
 (4) HCl lowers the solubility of H_2S in soln.
50. Prussian's blue is formed when Fe^{+3} ions are added to $\text{K}_4[\text{Fe}(\text{CN})_6]$ Prussian blue is
 (1) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (2) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
 (3) $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ (4) All
151. Turnbull's blue is formed when Fe^{+2} ions are added to $\text{K}_3[\text{Fe}(\text{CN})_6]_2$. Turnbull's blue is
 (1) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (2) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
 (3) $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ (4) All
152. If group IV the ppt. of $\text{Zn}(\text{OH})_2$ dissolves in excess of NaOH due to the formation of
 (1) Na_2ZnO_2 (2) NaZnO_2
 (3) Zn (4) Na_3ZnO_2
153. Br_2 water in NaOH soln. Oxidises $\text{Mn}(\text{OH})_2$ to a ppt. due to the formation of $\text{MnO}(\text{OH})_2$.
 (1) Black (2) Violet
 (3) Blue (4) White
155. Brown ppt. of $\text{MnO}(\text{OH})$ on boiling with PbO_2 and conc. HNO_3 yields a pink colouration on dilution due to the formation of
 (1) HMnO_4 (2) H_2MnO_4
 (3) $\text{Pb}(\text{MnO}_4)_2$ (4) PbMnO_3
155. A precipitate of would be obtained on adding HCl to a solution of As_2S_3 in yellow ammonium sulphide.
 (1) As_2S_3 (2) As_2S_5
 (3) As S (4) As S_2
156. A precipitate of would be obtained on adding HCl to a solution of SnS in yellow ammonium sulphide.
 (1) SnS (2) Sn_2S_3
 (3) SnS_2 (4) $(\text{NH}_4)_2\text{SnS}_2$
157. Which of the sulphides of group II is orange?
 (1) CuS (2) CdS
 (3) As_2S_3 (4) Sb_2S_3
158. Which of the sulphide of group II is not black or brownish black?
 (1) PbS (2) HgS
 (3) Bi_2S_3 (4) CdS or As_2S_3
159. Sometimes yellow turbidity appears while passing H_2S gas even in the absence of group II radicals. This is because of
 (1) Sulphur is present in the mixture as impurity
 (2) Group IV radicals are precipitated as sulphides
 (3) The oxidation of H_2S gas by some acid radicals
 (4) Group III radicals are precipitated as hydroxides
160. An inorganic substance gives black ppt. in group II which is dissolved in aqua regia. Evaporate off aqua regia and dilute it with water. To this few drops of ammonium thiocyanate and sodium acetate followed by $\text{Co}(\text{NO}_3)_2$ are added. A deep blue colour or ppt. is obtained. This is due to presence of
 (1) Hg^{2+} (2) Bi^{3+}
 (3) Pb^{2+} (4) Cd^{2+}
161. The sodium carbonate bead test in which Na_2CO_3 is used instead of borax. It is suitable to chromium and
 (1) Mn (2) Cu
 (3) Fe (4) Ni

162. Orange coloured sodium cobaltinitrite $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ is used for the detection of K^+ ions which gives ppt. due to the formation of Pot. Sod. Cobaltinitrite $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$
- (1) White (2) Orange
(3) Yellow (4) Brown

Multiple Correct Answers Type

Part-A (Analysis of Anions)

- When Zn reacts with conc. HNO_3 , then $\text{Zn}(\text{NO}_3)_2$ and NO_2 are formed; the reaction(s) involved in this process is/are
 - Redox reaction
 - Acid-base reaction
 - Ion exchange reaction
 - None
- Select the correct statement(s):
 - NaHCO_3 is sparingly soluble in water because it has massive H-bonding.
 - When BaCl_2 reacts with bicarbonate, then white ppt. of BaCO_3 is formed.
 - HgCl_2 is poisonous
 - Phenolphthalein is turned pink by soluble carbonate and colourless by soluble hydrogen carbonate.
- Which of the following anions may be identified by their ppt. reaction in aqueous solution?
 - CrO_4^{2-}
 - SO_4^{2-}
 - PO_4^{3-}
 - MnO_4^-
- Select the correct statement(s):
 - White ppt. of BaSO_3 and CaSO_3 is soluble in dil. HNO_3 , dil. HCl and CH_3COOH .
 - On standing, the precipitate BaSO_3 is slowly oxidised to sulphate and then becomes insoluble in dilute mineral acids.
 - When excess of SO_2 gas is passed into the solution of BaSO_3 and CaSO_3 , then white turbidity disappears.
 - The hydrogen carbonates of alkali metals are soluble in water, but are less soluble than the corresponding normal carbonates.
- Which of the following carbonates do not give metal oxide on heating?
 - CuCO_3
 - K_2CO_3
 - Na_2CO_3
 - MgCO_3
- Which of the following compounds are soluble in water?
 - CaC_2O_4
 - SrSO_4
 - BaCl_2
 - $(\text{NH}_4)_2\text{C}_2\text{O}_4$
- Which of the following halides are not soluble in water?
 - AgCl
 - AgBr
 - PbCl_2
 - AgF
- The brown ring test is performed for the qualitative detection of
 - Bromides
 - Iodides
 - Nitrates
 - Nitrite
- Which of the following salt does give positive test for nitrate ion?
 - KNO_3
 - NaNO_3
 - $\text{Mg}(\text{NO}_3)_2$
 - None of these
- Which of the following anions are easily removed from aqueous solution by precipitation?
 - Cl^-
 - SO_4^{2-}
 - NO_3^-
 - CO_3^{2-}
- A white ppt. is obtained when:
 - A solution of BaCl_2 is treated with Na_2CO_3
 - A solution of CaCl_2 is treated with Na_2SO_3
 - A solution of ZnSO_4 is treated with Na_2S
 - A solution of $\text{Pb}(\text{NO}_3)_2$ is treated with Na_2CrO_4
- Which pair would not be expected to form precipitate when solutions are mixed?
 - K^+ , SO_4^{2-}
 - Na^+ , S^{2-}
 - Ag^+ , NO_3^-
 - Al^{3+} , OH^-
- Reddish brown gas is obtained when the following are treated with conc. H_2SO_4 .
 - Br^-
 - NO_2^-
 - NO_3^-
 - SO_3^{2-}
- The correct statement(s) is/are with respect to chromyl chloride test:
 - Formation of lead chromate
 - Formation of chromyl chloride
 - Liberation of chloride
 - Formation of reddish-brown vapours.
- Nitrite (NO_2^-) interferes in the 'ring-test' of nitrate (NO_3^-). Some of the following reagents can be used for the removal of nitrite.
 - AgF
 - $(\text{NH}_2)_2\text{CS}$ (thiourea)
 - $\text{NH}_2\text{SO}_3\text{H}$ (sulphanilic acid)
 - None of these
- If (X) turns lime water milky, then X may be
 - CO_2
 - SO_2
 - NO_2
 - O_2
- If (X) turns acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution green, then X may be
 - SO_2
 - CO_2
 - NO_2^-
 - Fe^{2+}
- If (X) decolourises acidified KMnO_4 solution, then X may be
 - S^{2-}
 - SO_3^{2-}
 - Fe^{2+}
 - SO_2
- Which of the following ppt. (s) of sulphite ion have white colour?

- (1) Ag_2SO_3 (2) PbSO_3
(3) CaSO_3 (4) BaSO_3

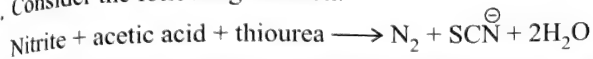
20. Which of the following gases have brown colour?

- (1) Br_2 (2) NO_2
(3) CO_2 (4) I_2

21. S^{2-} and SO_3^{2-} can be distinguished by using:

- (1) $(\text{CH}_3\text{COO})_2\text{Pb}$ (2) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$
(3) $\text{Cr}_2\text{O}_7^{2-}$ solution (4) CaCl_2

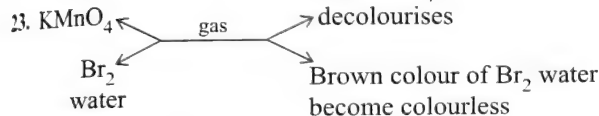
22. Consider the following reaction:



Formation of the product in the above reaction cannot be identified by

- (1) $\text{FeCl}_3/\text{dil. HCl}$ when blood-red colour appears
(2) $\text{FeCl}_3/\text{dil. HCl}$ when blue colour appears
(3) $\text{K}_2\text{Cr}_2\text{O}_7/\text{HCl}$ when green colour appears
(4) KMnO_4/HCl when colourless solution is formed

Purple colour
of KMnO_4
decolourises



The gas will be

- (1) CO_2 (2) SO_2
(3) H_2S (4) SO_3

24. Which of the following combinations in an aqueous medium will give a yellow ppt.?

- (1) $\text{AgNO}_3 + \text{NaBr}$ (2) $\text{Pb}(\text{CH}_3\text{COO})_2 + \text{Na}_2\text{CrO}_4$
(3) $\text{Fe}^{3+} + \text{SCN}^-$ (4) None of these

25. Which of the following nitrates are water soluble?

- (1) NaNO_3 (2) AgNO_3
(3) $\text{Hg}(\text{NO}_3)_2$ (4) LiNO_3

26. Which of the following reagents can be used to distinguish between SO_2 and CO_2 ?

- (1) Lime water
(2) Zinc nitroprusside paste in water
(3) Potassium iodate and starch
(4) Acidified potassium dichromate solution

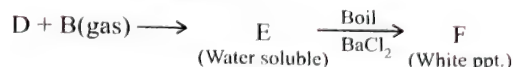
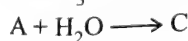
27. Each of these solutions is added to a mixture of aqueous solutions of iodide and chloroform (CHCl_3) separately. Which will give a positive test for iodine when the solutions are vigorously mixed?

- (1) NaCl solution (2) NaBr solution
(3) Chlorine water (4) Bromine water

28. For the lime water test, if the observations are positive for the unknown sample, then which of the following conclusion(s) is/are incorrect?

- (1) Sample has only NO_2 (2) Sample has only SO_3
(3) Sample has CO_2 and SO_2 (4) Sample has H_2S

29. $\text{CaCO}_3 \longrightarrow \text{A} + \text{B}(\text{gas})$



Select the correct option(s) for white ppt. shown in the above reactions:

- (1) CaCO_3 (2) MgCO_3
(3) BaCO_3 (4) Na_2CO_3

30. Which of the following statement(s) is/are correct?

- (1) In $\text{S}_2\text{O}_3^{2-}$, both sulphur are different in nature.
(2) Sodium acetate and lead acetate on heating giving same type of product, whereas Mn, Sn, Fe oxalate salt giving different type of products.
(3) Aqueous solution of OCl^- , S^{2-} and CO_3^{2-} are basic in nature.
(4) NO_2^- oxidises I^- whereas Br_2 and Cl_2 oxidise NO_2^- .

31. Which of the following anion(s) is/are interfering radicals?

- (1) BO_3^{3-} (2) F^-
(3) PO_4^{3-} (4) None of these

Part-B (Analysis of Cations)

32. Blue coloured compounds are obtained when

- (1) Fe^{2+} ions react with potassium ferricyanide
(2) Fe^{3+} ions react with potassium ferrocyanide
(3) Fe^{3+} ions react with potassium ferricyanide
(4) Fe^{2+} ions react with potassium ferrocyanide

33. Potassium ferrocyanide is used in the detection of

- (1) Fe^{2+} ions (2) Fe^{3+} ions
(3) Cu^{2+} ions (4) Cd^{2+} ions

34. Bromine is not recognised by its

- (1) Ability to turn starch iodide paper blue
(2) Ability to dissolve in CS_2 to give an orange colour to the organic layer
(3) Ability to dissolve in CS_2 to give a violet colour to the organic layer
(4) Ability to turn FeSO_4 solution black.

35. I_2 can be obtained from KI solution by the action of

- (1) Cl_2 (2) Br_2
(3) Soluble Cl^- (4) Soluble Br^-

36. Which of the following is not precipitated by H_2S in presence of conc. acid soln.

- (1) Cu^{2+} (2) Al^{3+}
(3) Sb^{3+} (4) Cd^{2+}

37. Which of the following is (are) soluble in excess of NaOH ?

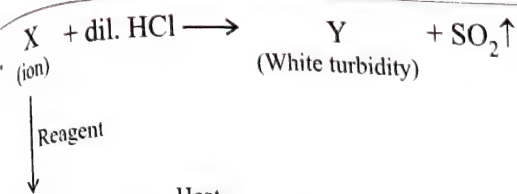
- (1) $\text{Cr}(\text{OH})_3$ (2) $\text{Fe}(\text{OH})_3$
(3) $\text{Al}(\text{OH})_3$ (4) $\text{Zn}(\text{OH})_2$

38. Select the correct statement(s):

- (1) When HgCl_2 reacts with carbonate ion, then basic mercury(II) carbonate is formed.

- (2) When HgCl_2 reacts with carbonate ion, then pH of solution highly increases.
- (3) The excess of carbonate acts as buffer reacting with the hydrogen ions formed in the reaction

$$\text{CO}_3^{2-} + 2\text{H}^+ \longrightarrow \text{CO}_2\uparrow + \text{H}_2\text{O}$$
- (4) White ppt. of MgCO_3 soluble in dil. H_2SO_4 .
39. Concentrated aqueous sodium hydroxide cannot separate a mixture of
 (1) Al^{3+} and Sn^{2+} (2) Al^{3+} and Fe^{3+}
 (3) Al^{3+} and Zn^{2+} (4) Zn^{2+} and Pb^{2+}
40. The metal ion(s) which is/are not precipitated when H_2S is passed with HCl is/are
 (1) Zn^{2+} (2) Ni^{2+}
 (3) Cd^{2+} (4) Mn^{2+}
41. An aqueous solution of a substance gives a white precipitate on treatment with dil. HCl which dissolves on heating. When H_2S is passed through the hot acidic solution, a black precipitate is obtained. The substances are not:
 (1) Hg_2^{2+} salt (2) Cu^{2+} salt
 (3) Ag^+ salt (4) Pb^{2+} salt
42. When H_2S gas is passed through HCl containing aqueous solution of CuCl_2 , HgCl_2 , BiCl_3 and CoCl_2 , then which of the following precipitate out?
 (1) CuS (2) HgS
 (3) Bi_2S_3 (4) CoS
43. Which of the following is/are soluble in excess of NaOH ?
 (X): $\text{Pb}(\text{OH})_2$ (Y): CuS ; (Z): $\text{Al}(\text{OH})_3$
 (1) X (2) Y
 (3) Z (4) None of these
44. Aqueous solution contains $\text{Zn}(\text{CH}_3\text{COO})_2$, $\text{Cd}(\text{CH}_3\text{COO})_2$ and $\text{Cu}(\text{CH}_3\text{COO})_2$. On passing H_2S gas, there is a precipitation of as sulphide.
 (1) Zn^{2+} (2) Cd^{2+}
 (3) Cu^{2+} (4) None of these
45. Which of the following pairs can be separated by H_2S in dil. HCl ?
 (1) Cu^{2+} and Cd^{2+} (2) Cu^{2+} and Ni^{2+}
 (3) Cu^{2+} and Zn^{2+} (4) Hg^{2+} and Al^{3+}
46. An inorganic salt solution on treatment with HCl will not give a white precipitate of which metal ions?
 (1) Hg_2^{2+} (2) Hg^{2+}
 (3) Zn^{2+} (4) Al^{3+}
47. Ammonium molybdate is used to test the radical:
 (1) PO_4^{3-} (2) AsO_4^{3-}
 (3) Cu^{2+} (4) Ag^+
48. Which of the following chlorides are water soluble?
 (1) AgCl (2) Hg_2Cl_2
 (3) HgCl_2 (4) NaCl
49. Which of the following metal sulphide is soluble in hot and dil. HNO_3 ?
 (1) Ag_2S (2) PbS
 (3) CdS (4) HgS
50. Which of the following ppt. is soluble in dil. HNO_3 and NH_3 solution?
 (1) $\text{Ag}_2\text{S}_2\text{O}_3$ (2) Ag_2CO_3
 (3) Ag_2SO_3 (4) AgI
51. Which of the following ppt. is insoluble in NH_3 solution?
 (1) AgI (2) Ag_2S
 (3) AgCl (4) AgBr
52. Which of the following will be completely or partially dissolved in NH_4OH ?
 (1) AgCl (2) AgBr
 (3) BaSO_4 (4) AgI
53. Interfering radicals interfere the test of
 (1) Group III radicals only
 (2) Group III radicals or downward
 (3) Cations which are present in group II filtrate
 (4) None of the above
54. Which of the following is/are correct for potassium ferrocyanide?
 (1) It gives a brown precipitate with Cu^{2+} ions
 (2) It gives a red precipitate of mixed salt with Cd^{2+} ions
 (3) If in excess gives a white precipitate with Zn^{2+}
 (4) It develops a deep red colouration with Fe^{3+}
55. Which of the following statements is not correct?
 (1) Lead(II) chloride is soluble in hot water and reappears on cooling
 (2) In dilute HCl , the solubility of PbCl_2 is higher than the hot water
 (3) In concentrated HCl , PbCl_2 is insoluble
 (4) Lead(II) chloride forms the complex with conc. HCl
56. Which of the following compounds are having white ppt.?
 (1) $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ (2) $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$
 (3) ZnS (4) $\text{Zn}(\text{OH})_2$
57. Which of the following compounds do not have white colour in the form of ppt.?
 (1) Bi_2S_3 (2) $\text{Co}[\text{Hg}(\text{SCN})_4]$
 (3) CdS (4) BiI_3
58. Out of Cu^{2+} , Ni^{2+} , Co^{2+} and Mn^{2+} , of those that dissolve in dil. HCl , only one gives a precipitate when H_2S is passed. Identify the corresponding order which do not give precipitation:
 (1) Ni^{2+} (2) Cu^{2+}
 (3) Co^{2+} (4) Mn^{2+}
59. Which of the following sulphides are soluble only in aqua regia?
 (1) NiS (2) CoS
 (3) HgS (4) CdS



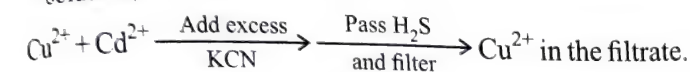
White ppt. $\xrightarrow[\text{aq. suspension}]{\text{Heat}}$ Black ppt.

Which of the following cation may be present in white ppt?

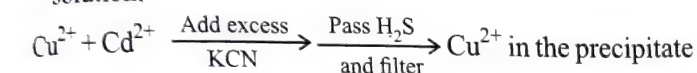
- (1) Pb^{2+} (2) Hg^{2+}
(3) Ag^{\oplus} (4) Bi^{3+}

Which of the following is/are correct process for the separation of given ions?

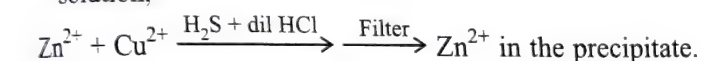
- (1) Cu^{2+} from the mixture of Cu^{2+} and Cd^{2+} in aqueous solution,



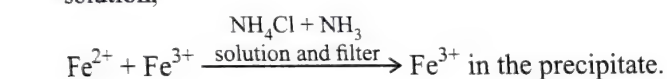
- (2) Cu^{2+} from the mixture of Cu^{2+} and Cd^{2+} in aqueous solution,



- (3) Zn^{2+} from the mixture of Zn^{2+} and Cu^{2+} in aqueous solution,



- (4) Fe^{3+} from the mixture of Fe^{2+} and Fe^{3+} in aqueous solution,



Part-C (Dry Test)

62. Flame test is not given by

- (1) Mg^{2+} ions (2) Ba^{2+} ions
(3) Be^{2+} ions (4) Ca^{2+} ions

63. Borax bead test is not given by

- (1) Copper salts (2) Nickel salts
(3) Aluminium salts (4) Magnesium salts

64. Which of the following respond to borax bead test?

- (1) Nickel salts (2) Copper salts
(3) Cobalt salts (4) Aluminium salts

65. In borax bead test, which compound(s) is/are not formed?

- (1) Orthoborate (2) Metaborate
(3) Double oxide (4) Tetraborate

66. Which of the following cation(s) will turn blue in oxidising flame?

- (1) Co^{2+} (2) Cr^{3+}
(3) Ni^{2+} (4) Cu^{2+}

67. Which of the following substances are green?

- (1) $\text{Fe}(\text{BO}_2)_3$ (2) Cu
(3) $\text{Cr}(\text{BO}_2)_3$ (4) $\text{Co}(\text{BO}_2)_2$

68. Borax bead test is given by

- (1) Co^{2+} (2) Zn^{2+}
(3) Cu^{2+} (4) Ni^{2+}

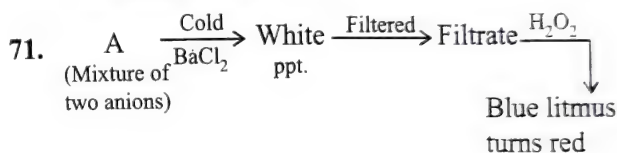
69. Colourless salt (X) $\xrightarrow{\Delta}$ (Y) $\xrightarrow{\text{Cu}^{2+}, \Delta}$ coloured bead (Z)
(X) can be

- (1) Borax (2) Microcosmic salt
(3) Copper sulphate (4) None of these

Part-D (Miscellaneous)

70. Select the correct statement(s):

- (1) Normal and polysulphides of alkali metals are soluble in water.
(2) The sulphides of aluminium, chromium and magnesium can only be prepared under dry conditions as they are completely hydrolysed by water.
(3) When filter paper is moistened with a solution of sodium nitroprusside made alkaline with sodium hydroxide or ammonia solution, a purple colouration is produced with free hydrogen sulphide.
(4) Thiosulphate salts of Pb, Ag and Ba are insoluble and dissolve in excess of sodium thiosulphate solution forming thiosulphate.



Mixture of A contains:

- (1) CO_3^{2-} , HCO_3^{\ominus} anions (2) CO_3^{2-} , HSO_3^{\ominus} anions
(3) SO_3^{2-} , HSO_3^{\ominus} anions (4) None of these

72. Which of the following statement(s) is/are incorrect?

- (1) Manganese salts give a violet borax bead test in reducing flame.
(2) From a mixed precipitate of AgCl and AgI , ammonia solution dissolves only AgCl .
(3) Ferric ions give a deep green precipitate on adding potassium ferrocyanide solution.
(4) On boiling the solution having K^{\oplus} , Ca^{2+} and HCO_3^{\ominus} ions, we get a precipitate of $\text{K}_2\text{Ca}(\text{CO}_3)_2$.

73. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are)

- (1) NH_4NO_3 (2) NH_4NO_2
(3) NH_4Cl (4) $(\text{NH}_4)_2\text{SO}_4$

74. Which of the following statements is/are not true?

- (1) $\text{Fe}^{2+}_{(\text{aq})}$ gives brown colour with NH_4SCN .
(2) $\text{Fe}^{3+}_{(\text{aq})}$ gives blood-red colour with NH_4SCN .
(3) $\text{Fe}^{2+}_{(\text{aq})}$ yields orange colour with $\text{K}_3\text{Fe}(\text{CN})_6$.
(4) Ag^{\oplus} reacts with CO_3^{2-} then black ppt. is formed.

75. Which of the following react with dil. H_2SO_4 ?

- (1) CaCO_3 (2) KNO_2
(3) Na_2S (4) BaCl_2

76. Conc. H_2SO_4 will not give any gas with:

- (1) ZnSO_4 (2) barium phosphate
(3) magnesium borate (4) sodium oxalate

77. Select the correct statement(s):

- (1) All carbonate salts are soluble except carbonate salts of alkali metals and $(\text{NH}_4)_2\text{CO}_3$.
(2) All bicarbonate salts are soluble except NaHCO_3 which is sparingly soluble.
(3) All sulphite salts are insoluble except sulphite salts of alkali metals and $(\text{NH}_4)_2\text{SO}_3$.
(4) All MnO_4^- salts are insoluble.

78. Select the correct statement(s):

- (1) White ppt. of BaCO_3 and CaCO_3 is soluble in dil. HNO_3 , dil. HCl , CH_3COOH and soda water.
(2) White ppt. of PbCO_3 is soluble in dil. HNO_3 , dil. HCl , excess of NaOH and CH_3COOH .
(3) White ppt. of Ag_2CO_3 is soluble in dil. HNO_3 and NH_3 solution.
(4) HCN and H_3BO_3 are stronger acids than H_2CO_3 .

79. Select the correct statement(s):

- (1) HCl is not used as acid for titration of SO_2 .
(2) Soda extract solution is very useful when any insoluble salt is present in a given mixture.
(3) SO_2 gas is identified by a filter paper moistened with potassium iodate and starch solution.
(4) When zinc and sulphuric acid react with sulphite, then hydrogen sulphide gas is evolved which may be detected by holding lead acetate paper to the mouth of the test tube.

80. Select the correct statement(s):

- (1) $\text{Ag}_2\text{S}_2\text{O}_3$ appears as white precipitate when $\text{Na}_2\text{S}_2\text{O}_3$ reacts with AgNO_3 .
(2) $\text{Ag}_2\text{S}_2\text{O}_3$ is unstable turning black on standing due to formation of Ag_2S .
(3) $\text{S}_2\text{O}_3^{2-}$ can form soluble complex $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ with Ag^+ .
(4) $\text{Na}_2\text{S}_2\text{O}_3$ is used in photography.

81. Which of the following complex(s) will have blue colour solution or ppt.?

- (1) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ (2) $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$
(3) $\text{Co}[\text{Hg}(\text{SCN})_4]$ (4) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$

82. Which of the following statement(s) is(are) true?

- (1) Soluble bicarbonates give white precipitate with MgCl_2 in cold
(2) Soluble calcium bicarbonates give white precipitate with dilute ammonia solution followed by MgSO_4 .
(3) Bicarbonates are generally soluble in water.
(4) $\text{Hg}(\text{II})$ chloride forms a reddish-brown precipitate in a solution of soluble carbonate.

83. Which of the following statement(s) is(are) correct?

- (1) Soluble sulphide gives black precipitate with AgNO_3 solution which is soluble in hot dilute nitric acid.

(2) Soluble sulphide produces a yellow precipitate with a suspension of cadmium carbonate.

(3) Sulphide ion reacts with sodium nitroprusside and gives a purple colouration.

(4) Free H_2S gas forms white precipitate with tetrahydroxido plumbate(II) solution.

84. Which of the following statement(s) is(are) incorrect?

(1) In thiourea test for nitrite, a green coloured solution is obtained.

(2) It is not necessary to carry out the chromyl chloride test in a dry test tube.

(3) In PbNO_3 , the brown ring test can be performed with its water extract.

(4) Suspension of CdCO_3 gives black ppt. with sodium sulphide solution.

85. Which of the following is(are) correct?

(1) $[\text{Al}(\text{OH})_4]^- + \text{NH}_4^+ \xrightarrow{\text{Slightly heat}} \text{white precipitate and liberation of ammonia}$

(2) $\text{Pb}^{2+} + 2\text{Br}^- \longrightarrow \text{Red precipitate}$

(3) BiI_3 (black precipitate) + $\text{H}_2\text{O}(\text{l}) \xrightarrow{\Delta} \text{Orange turbidity}$

(4) $\text{Fe}^{3+} + \text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow \text{Blue precipitate}$

86. Pick out the correct statement(s):

(1) Golden yellow PbI_2 dissolves in hot water to give a colourless solution.

(2) Ba^{2+} and Ca^{2+} ions can be separated by adding SO_4^{2-} ion in acetic acid medium.

(3) Salts of calcium, copper and nickel give a green flame colour.

(4) The sulphide ion gives with alkaline sodium nitroprusside, a violet colour.

87. Which of the following statement(s) is(are) true?

(1) Cu^{2+} salts form soluble complex with excess KCN .

(2) Cu^{2+} salts form soluble complex with aqueous ammonia.

(3) Cu^{2+} salts form soluble complex with KI .

(4) A piece of iron or zinc when placed in Cu^{2+} salt solution, precipitates copper.

88. Which of the following statement(s) is(are) true?

(1) In a mixture of Sr^{2+} and Ca^{2+} , ammonium sulphate precipitates only Sr^{2+} as SrSO_4 but CaSO_4 dissolves in ammonium sulphate forming a soluble complex.

(2) Barium chromate is insoluble in dilute acetic acid.

(3) $\text{Cr}(\text{OH})_3$ is soluble in NaOH and Br_2 water while $\text{Fe}(\text{OH})_3$ is insoluble.

(4) Cu and Cd separation is based upon the fact that in presence of excess KCN , only Cd is precipitated as sulphide on passing H_2S .

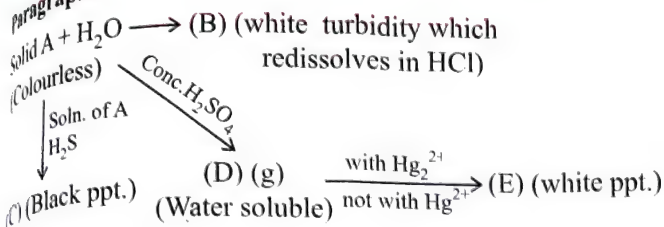
89. Potassium cyanide is used for separating

(1) Co^{2+} and Ni^{2+} (2) Cu^{2+} and Cd^{2+}

(3) Mn^{2+} and Zn^{2+} (4) Ba^{2+} and Ca^{2+}

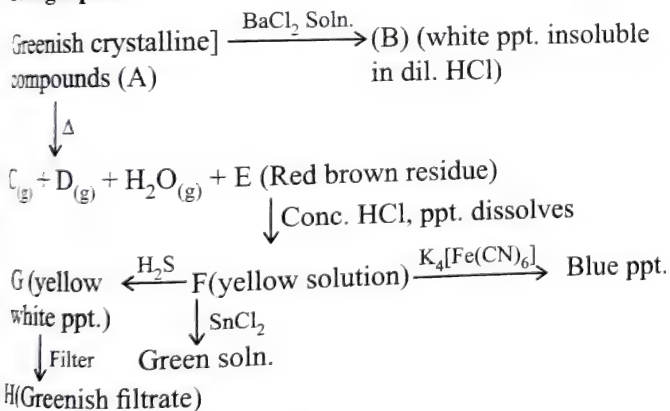
Linked Comprehension Type

Paragraph 1



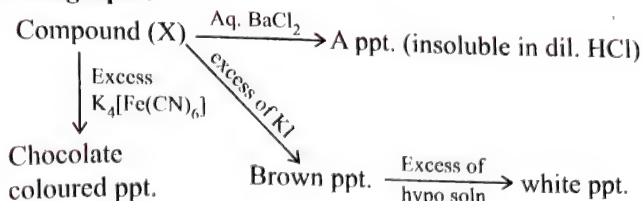
- Identify A.
 (1) BiOCl (2) Bi₂S₃
 (3) BiCl₃ (4) BaSO₄
- Identify B.
 (1) BiOCl (2) BaS
 (3) BiCl₃ (4) None of these
- Identify C.
 (1) BiOCl (2) Bi₂S₃
 (3) BiCl₃ (4) H₂S
- Identify D.
 (1) Br₂ (2) HCl
 (3) I₂ (4) Cl₂
- Identify E.
 (1) Hg₂(NO₃)₂ (2) HCl
 (3) Hg₂Cl₂ (4) HNO₃

Paragraph 2



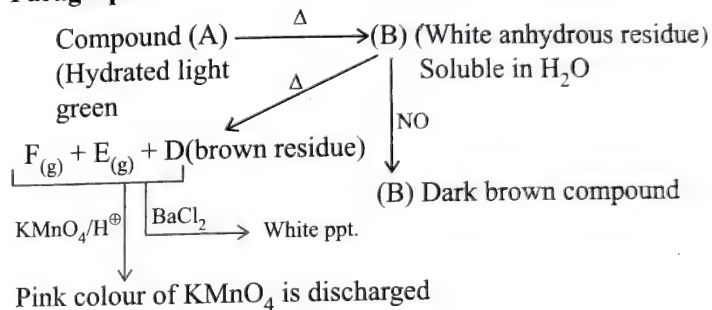
- Identify compound A.
 (1) ZnSO₄·7H₂O (2) FeSO₄·7H₂SO₄
 (3) MgSO₄·7H₂O (4) CuSO₄·5H₂O
- Gases C and D are
 (1) SO₂, SO₃ (2) SO₃, CO₂
 (3) NO₂, MgO (4) ZnO, SO₃
- Identify yellow solution F.
 (1) Fe₂O₃ (2) FeCl₃
 (3) ZnCl₂ (4) CuCl
- Identify G.
 (1) SO₂ (2) ZnS
 (3) S (4) FeS

Paragraph 3



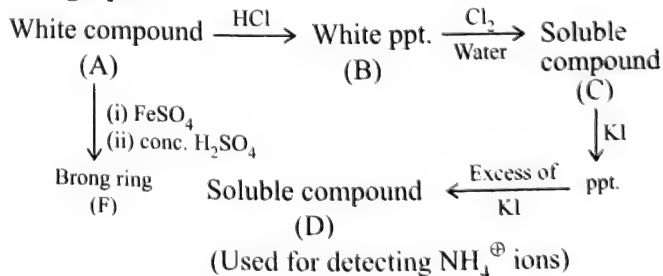
- Identify X.
 (1) CuSO₄ (2) BaSO₄
 (3) BaCl₂ (4) NaI
- What is the formula of chocolate coloured ppt.?
 (1) Fe₄[Fe(CN)₆] (2) Cu₂[Fe(CN)₆]
 (3) Cu₂[Fe(CN)₄] (4) Cu(CN)₂
- What is the formula of brown ppt.?
 (1) Cu₂I₂ (2) Cu₂I₂ + I₃[⊖]
 (3) CuI₂ (4) CuSO₄

Paragraph 4



- Identify C.
 (1) [Fe(H₂O)₅NO]SO₄ (2) Na₂SO₄
 (3) Na₂[Fe(CN)₅NO] (4) Fe₄[Fe(CN)₆]₃
- Identify B.
 (1) ZnSO₄ (2) CuSO₄
 (3) MgSO₄ (4) FeSO₄
- Identify D.
 (1) ZnO (2) FeO
 (3) Fe₂O₃ (4) CuO

Paragraph 5



- Compound (A) is
 (1) HgI₂ (2) K₂HgI₄
 (3) Hg(NO₃)₂ (4) Hg₂(NO₃)₂
- Oxidation state of Fe in compound (F) is
 (1) +1 (2) +2
 (3) +3 (4) +4
- (D) + (NH₄)₂SO₄ → brown ppt. (G) in basic medium

Hence, compound (G) is

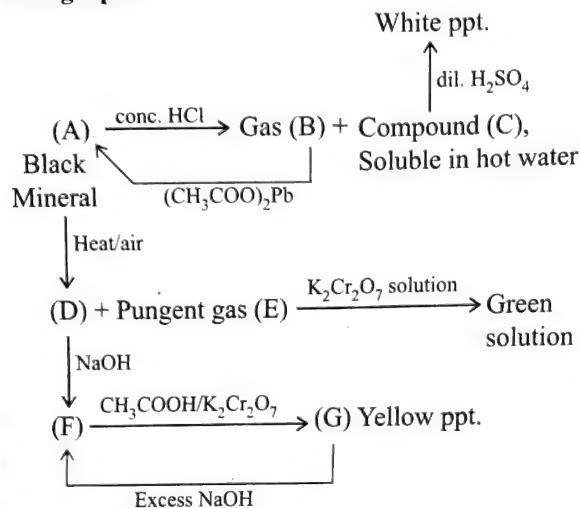
- (1) HgI_2 (2) NH_4I
 (3) $\left[\text{Hg} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{NH}_2 \end{array} \text{Hg} \right] \text{I}$ (4) $\text{Hg}(\text{NH}_2)\text{I}$

19. White ppt. (B) + $\text{NH}_3 \rightarrow$ Black ppt. (H).

Hence, (H) is due to the formation of

- (1) $\text{Hg}(\text{NH}_2)\text{Cl}$ (2) Hg
 (3) $\text{Hg}(\text{NH}_2)\text{Cl} + \text{Hg}$ (4) $\text{Hg}(\text{NH}_2)_2$

Paragraph 6



20. Gas (B) on passing through CdSO_4 solution will give

- (1) Black ppt. (2) Yellow ppt.
 (3) Orange ppt. (4) No ppt.

21. Compound (A), (B) and (E) are respectively

- (1) CuS , H_2S , SO_2 (2) PbS , H_2S , SO_2
 (3) PbS , H_2S , SO_3 (4) ZnS , H_2S , SO_2

22. Compound (C) and (D) are respectively

- (1) PbO , PbCl_2 (2) PbCl_2 , PbO
 (3) PbO , PbO_2 (4) PbS , PbO

Paragraph 7

i. (A) $\xrightarrow[\Delta]{\text{NaOH}}$ (B) (g) $\xrightarrow{\text{HCl}}$ White fumes.

ii. After (B) is expelled completely, resultant alkaline solution again gives gas (B) on heating with zinc.

iii. (A) $\xrightarrow{\Delta} \text{N}_2\text{O} + \text{H}_2\text{O}$

23. Identify A.

- (1) NH_4NO_2 (2) NH_4NO_3
 (3) HCl (4) Na_2SO_4

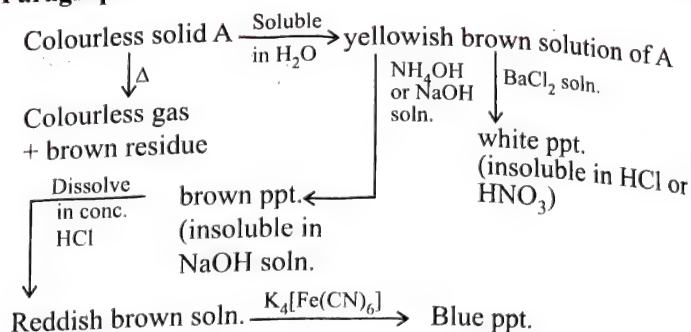
24. Identify B.

- (1) SO_2 (2) NH_3
 (3) N_2O (4) NO_2

25. What is the formula of white fumes?

- (1) NH_4NO_3 (2) NH_4Cl
 (3) NH_4NO_2 (4) NH_3

Paragraph 8



26. Identify A.

- (1) FeSO_4 (2) $\text{Fe}_2(\text{SO}_4)_3$
 (3) Fe_2O_3 (4) FeO

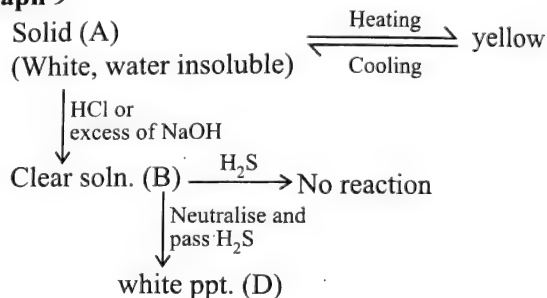
27. What is the formula of brown ppt?

- (1) $\text{Fe}(\text{OH})_3$ (2) $\text{Fe}(\text{OH})_2$
 (3) FeCl_3 (4) None of these

28. Which of the following complex is formed when A reacts with $\text{K}_4[\text{Fe}(\text{CN})_6]$?

- (1) Prussian blue (2) Turnbull's blue
 (3) Brown ring complex (4) Sodium nitroprusside

Paragraph 9



29. Identify A.

- (1) ZnS (2) ZnO
 (3) MgO (4) FeO

30. Identify B.

- (1) FeCl_2 (2) NiCl_2
 (3) ZnCl_2 (4) FeCl_3

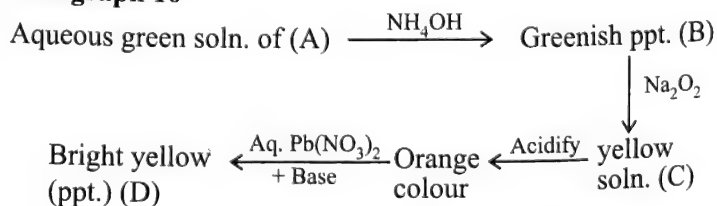
31. Identify C.

- (1) Na_2ZnO_2 (2) $\text{Zn}(\text{OH})_2$
 (3) $\text{Fe}(\text{OH})_3$ (4) $\text{Fe}(\text{OH})_2$

32. Identify D.

- (1) ZnO (2) ZnS
 (3) FeO (4) FeS

Paragraph 10



33. Identify A.

- (1) AlCl_3 (2) $\text{Cr}(\text{OH})_3$
 (3) CrCl_3 (4) None of these

34. Identify B.

- (1) CrCl_3 (2) $\text{Cr}(\text{OH})_3$
 (3) $\text{Mn}(\text{OH})_2$ (4) CrO_4^{2-}

35. Identify C.

- (1) $\text{Na}_2\text{Cr}_2\text{O}_7$ (2) Na_2CrO_4
 (3) Na_2MnO_4 (4) NaMnO_4

36. Identify D.

- (1) PbS (2) PbI_2
 (3) PbCrO_4 (4) $\text{Zn}(\text{OH})_2$

Paragraph 11

Dark brown solid (A) $\xrightarrow{\text{conc. H}_2\text{SO}_4}$ Brown gas (B)
 $\xrightarrow{\text{H}_2\text{O} + \text{dil. NaOH or NH}_4\text{OH}}$ Red brown ppt. (C) insoluble in excess of either reagent
 $\xrightarrow{\text{H}_2\text{O} + \text{AgNO}_3}$ Cream coloured (light yellow) ppt. (D), insoluble in dil. HNO_3

37. Identify A.

- (1) $\text{Fe}(\text{NO}_2)_3$ (2) ZnBr_2
 (3) FeBr_3 (4) ZnCl_2

38. Identify B.

- (1) Cl_2 (2) Br_2
 (3) NO_2 (4) I_2

39. Identify C.

- (1) $\text{Fe}(\text{OH})_3$ (2) Fe_2O_3
 (3) FeO (4) FeS

40. Identify D.

- (1) AgCl (2) AgF
 (3) AgBr (4) None of these

Paragraph 12

- i. (A) $\xrightarrow{\Delta}$ glassy transparent bead (B) on platinum wire.
 (B) + $\text{CuSO}_4 \longrightarrow$ coloured bead (C).
 ii. (A) + conc. H_2SO_4 + $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{ignite}}$ green flame (D)
 iii. Aqueous solution (A) is alkaline.

41. Identify A.

- (1) $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ (2) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
 (3) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (4) None of these

42. What is the formula of glassy bead (B)?

- (1) NaPO_3 (2) NaBO_2
 (3) $\text{NaBO}_2 + \text{B}_2\text{O}_3$ (4) None of these

43. Identify C.

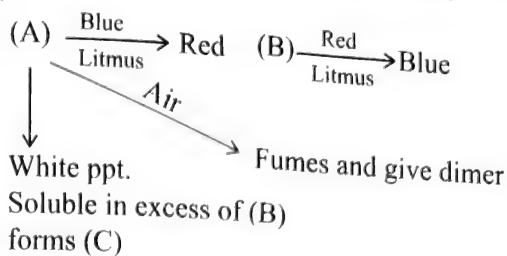
- (1) $\text{Cu}_3(\text{PO}_4)_2$ (2) CuSO_4
 (3) $\text{Cu}(\text{BO}_2)_2$ (4) None of these

44. Identify D.

- (1) $(\text{CH}_3)_3\text{BO}_3$ (2) $(\text{C}_2\text{H}_5)_3\text{BO}_3$
 (3) H_3BO_3 (4) None of these

Paragraph 13

A colourless mixture of two salts (A) and (B) [excess] is soluble in H_2O .



45. Identify A.

- (1) AlCl_3 (2) ZnCl_2
 (3) FeCl_3 (4) None of these

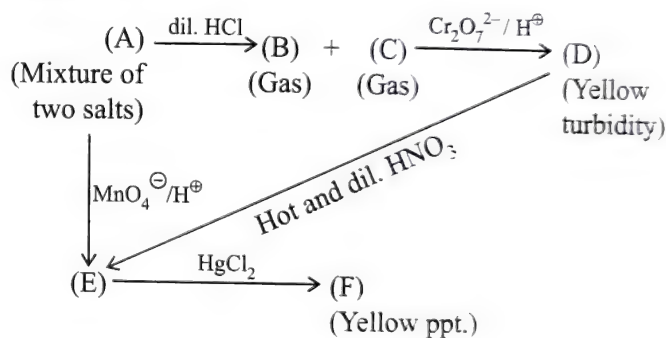
46. Identify B.

- (1) $\text{Al}(\text{OH})_3$ (2) $\text{Zn}(\text{OH})_2$
 (3) NaOH (4) None of these

47. Identify C.

- (1) Na_2ZnO_2 (2) NaAlO_2
 (3) Na_2SnO_2 (4) None of these

Paragraph 14



48. Find the anion(s).

- (1) SO_3^{2-} (2) $\text{SO}_3^{2-}, \text{S}^{2-}$
 (3) $\text{SO}_3^{2-}, \text{CO}_3^{2-}$ (4) $\text{S}_2\text{O}_3^{2-}$

49. Find out (E).

- (1) S^{2-} (2) CO_3^{2-}
 (3) $\text{S}_2\text{O}_3^{2-}$ (4) SO_4^{2-}

50. Find out (F).

- (1) $\text{HgSO}_4 \cdot 2\text{HgO}$ (2) $\text{HgSO}_4 \cdot 3\text{HgO}$
 (3) HgSO_4 (4) $\text{Hg}_2\text{SO}_4 \cdot 3\text{HgO}$

Paragraph 15

Cations are classified into various groups on the basis of their behaviour against some reagents. The group reagents used for the classification of most common cations are HCl , H_2S , NH_4OH , $(\text{NH}_4)_2\text{CO}_3$. Classification is based on whether a cation reacts with these reagents by the formation of precipitates or not.

51. Which one among the following pairs of ions cannot be separated by H_2S in the presence of dilute hydrochloric acid?

- (1) $\text{Bi}^{3+}, \text{Cd}^{2+}$ (2) $\text{Al}^{3+}, \text{Hg}^{2+}$
 (3) $\text{Zn}^{3+}, \text{Cu}^{2+}$ (4) $\text{Ni}^{2+}, \text{Cu}^{2+}$

52. An aqueous solution contains Hg^{2+} , Hg_2^{2+} , Pb^{2+} and Cd^{2+} . The addition of 2M HCl will precipitate:

- (1) HgCl_2 only (2) PbCl_2 only
 (3) PbCl_2 and Hg_2Cl_2 (4) PbCl_2 and CdCl_2

53. An aqueous solution which is slightly acidic contains cations Fe^{3+} , Zn^{2+} and Cu^{2+} . The reagent when added in excess to this solution would identify the separate Fe^{3+} ion in one step is

- (1) 2M HCl (2) 6M NH_3
 (3) 6M NaOH (4) H_2S gas

Paragraph 16

The reagents like AgNO_3 , $\text{K}_4[\text{Fe}(\text{CN})_6]$, KCNS , KI , K_2CrO_4 Nessler's reagent, etc., find extensive and very important application in qualitative analysis because these reagents form different types of products with different cations. For example, KI forms yellow precipitate with Pb^{2+} but it forms red precipitate with Hg^{2+} . Hence, these reagents are widely used in the qualitative analysis of inorganic salts.

54. Which of the following is not correctly matched?

- (1) $\text{Ag}^{\oplus} + \text{S}_2\text{O}_3^{2-} \longrightarrow$ White ppt.
 (2) $\text{Pb}^{2+}_{(\text{aq})} + 2\text{Cl}^{-}_{(\text{aq})} \longrightarrow$ Black precipitate
 (3) BiI_3 (Black precipitate) + $\text{H}_2\text{O}(\text{l}) \xrightarrow{\Delta}$ Orange turbidity.
 (4) $\text{Ca}^{2+}_{(\text{aq})} + \text{K}_4[\text{Fe}(\text{CN})_6]_{(\text{aq})} \longrightarrow$ White precipitate

55. Which of the following cations (i.e., basic radicals) forms coloured (not white) precipitates with aqueous solution of potassium iodide but precipitate does not dissolve in excess of reagent?

- (1) Hg^{2+} (2) Hg_2^{2+}
 (3) Bi^{3+} (4) Cu^{2+}

56. Which of the following hydroxide does not dissolve in ammonia solution but dissolves in sodium hydroxide?

- (1) $\text{Zn}(\text{OH})_2$ (2) $\text{Cd}(\text{OH})_2$
 (3) $\text{Cu}(\text{OH})_2$ (4) $\text{Al}(\text{OH})_3$

Paragraph 17

More than one correct

NH_3 solution was added to four sample solution in different test tube and found the following observation about the precipitate.

- (a) White ppt. which is soluble in excess of NH_3 solution.
 (b) On heating white ppt. obtained from (a) produces a compound which is white in cold but yellow on heating.
 (c) The cation present in (b) forms white ppt. with hypo solution which gives black ppt. on heating.
 (d) The cation present in (c) forms soluble complex with excess of NH_3 solution.
57. White ppts. in (a), (b) and (c), respectively, obtained are
 (1) $\text{Zn}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{HgO} \cdot \text{Hg}(\text{NH}_2)\text{NO}_3$
 (2) $\text{Cd}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{HgO} \cdot \text{Hg}(\text{NH}_2)\text{NO}_3$
 (3) $\text{HgO} \cdot \text{Hg}(\text{NH}_2)\text{NO}_3$, $\text{Zn}(\text{OH})_2$, $\text{Cd}(\text{OH})_2$
 (4) $\text{Al}(\text{OH})_3$, $\text{Zn}(\text{OH})_2$, $\text{Pb}(\text{OH})_2$
58. The solution initially present in (a) + H_2S (basic medium) gives ppt., then (a) may have

- (1) Zn^{2+} (2) Cd^{2+}
 (3) Co^{2+} (4) Ni^{2+}

59. White ppt. in (c) and the soluble complex formed from white ppt. with the hypo solution is/are

- (1) $\text{Pb}(\text{OH})_2$, $[\text{Pb}(\text{S}_2\text{O}_3)_2]^{2-}$
 (2) Ag_2O , $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{2-}$
 (3) $\text{HgO} \cdot \text{Hg}(\text{NH}_2)\text{NO}_3$, $[\text{Hg}(\text{S}_2\text{O}_3)_2]^{2-}$
 (4) None of these

Paragraph 18

(A) is a colourless solid; it melts when heated and gives off a gas (B) which is supporter of combustion. If heating is continued, the whole of the solid disappears. When (A) is heated with an aqueous NaOH solution, an alkaline gas (C) is evolved. When gas (B) is heated with sodamine, a colourless solid (D) is formed. When (D) is heated with dil. H_2SO_4 , a colourless liquid (F) is formed.

60. The compound E has

- (1) Linear structure (2) Bent structure
 (3) Tetrahedral structure (4) None of these

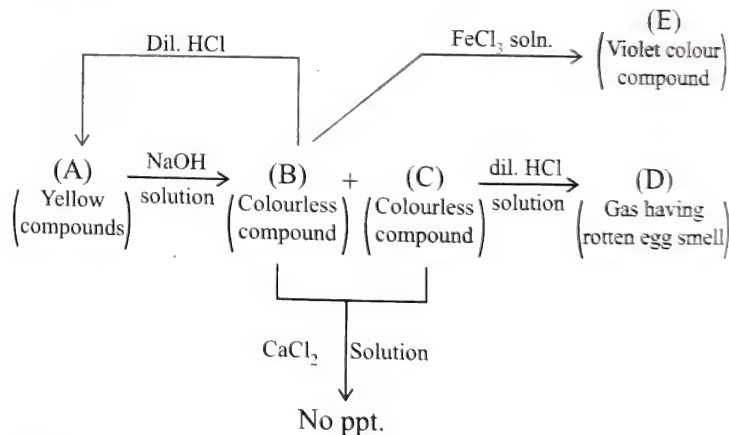
61. The name of compound E is

- (1) Ammonia (2) Hydrazoic acid
 (3) Hydrogen amide (4) None of these

62. The compound C has

- (1) Linear geometry (2) Pyramidal
 (3) Tetrahedral (4) None of these

Paragraph 19



63. Compound (B) on strong heating produces compound(s) which has/have

- (1) Chain structure (2) Tetrahedral structure
 (3) Both (a) and (b) (4) None of these

64. Which of the following statements is/are correct for gas (D)?

- I. It has the state of hybridisation sp^3 .
 II. Gas can be identified by CaCl_2 solution.
 III. Gas can be identified by $\text{Pb}(\text{OAc})_2$ solution.
 IV. Gas can be identified by passing through sodium nitroprusside solution.

- (1) I, IV (2) I, III
 (3) III only (4) I, II, IV

65. Compound (B) on reaction with $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ gives a coloured complex exhibiting

- (1) Optical isomerism (2) Geometrical isomerism
(3) Linkage isomerism (4) No isomerism

Paragraph 20

A colourless solid (A) when placed into water produces a heavy white turbidity of (B). Solid (A) gives a clear solution in conc. HCl. When HCl solution is added to large amounts of water, (B) forms again. (B) dissolves in dilute HCl. When H_2S is passed through a suspension of (A) or (B), a black precipitate (C) forms, (C) is insoluble in yellow ammonium sulphide $(\text{NH}_4)_2\text{S}$. Conc. H_2SO_4 added to solid (A) liberates gas (D). Gas (D) is water-soluble and gives white precipitate with mercuric salts (E) and not mercuric salts. The black precipitate (C) dissolves in HNO_3 (1:1) to give a solution to which H_2SO_4 is added followed by addition of NH_4OH when a white precipitate (F) is formed. (E) gives a black ppt. (G) with solution of sodium stannite.

66. When compound (E) reacts with NH_4OH , then product is a

- (1) White ppt. (2) Black ppt.
(3) Yellow ppt. (4) Green ppt.

67. Compound (C) is also formed by the following reaction:

- (1) $\text{Ba}^{2+} + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{E}$ (2) $\text{Bi}^{3+} + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{E}$
(3) $\text{Bi}_2\text{S}_2\text{O}_3 \xrightarrow{\Delta} \text{E}$ (4) None of these

68. Compound (B) is not soluble in

- (1) Tartaric acid (2) HCl
(3) HNO_3 (4) H_2SO_4

Matrix Match Type

1. Match the column:

Column I	Column II
a. $\text{Fe}^{3+} + \text{SO}_2 \longrightarrow$	p. White ppt.
b. $\text{Pb}^{2+} + \text{Na}_2\text{S} \longrightarrow$	q. Black ppt.
c. $\text{SO}_3^{2-} + \text{Pb}(\text{NO}_3)_2 \longrightarrow$	r. Yellow ppt.
d. $\text{PbSO}_3 + \text{O}_2 \xrightarrow{\text{Boil}} \longrightarrow$	s. Green colouration
e. $\text{Cd}^{2+} + \text{Na}_2\text{S} \longrightarrow$	

2. Match the colour of precipitates listed in column (I) with the reagent(s) listed in column (II):

Column I	Column II
a. Bi^{3+} gives black precipitate with	p. Saturated solution of H_2S in water
b. Cu^{2+} gives black precipitate with	q. Potassium thiocyanate solution
c. Zn^{2+} gives white precipitate with	r. Potassium iodide solution
d. Ag^+ gives white precipitate with	s. Potassium ferrocyanide solution

3. Match the column:

Column I	Column II
a. Fe^{2+} reacts with $\text{K}_3[\text{Fe}(\text{CN})_6]$	p. Cherryred ppt.
b. Fe^{3+} reacts with $\text{K}_4[\text{Fe}(\text{CN})_6]$	q. Turnbull's blue
c. Ni^{2+} reacts with DMG	r. Prussian blue
d. Cu^{2+} reacts with NH_3 solution	s. Blue solution

4. Match the column:

Column I	Column II
a. $\text{Na}_2\text{S} + \text{Hg}(\text{NO}_3)_2 \longrightarrow$	p. Pale green solution
b. $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \longrightarrow$	q. Black ppt.
c. $\text{Na}_2\text{S}_2\text{O}_3 + \text{BaCl}_2 \longrightarrow$	r. Finally purple colour
d. $\text{Na}_2\text{S}_2\text{O}_3 + \text{Pb}(\text{NO}_3)_2 \longrightarrow$	s. White ppt.
e. $\text{Fe}^{3+} + \text{S}_2\text{O}_3^{2-} \longrightarrow$	

5. Match the column:

Column I	Column II
a. $\text{K}_4[\text{Fe}(\text{CN})_6]$	p. Produces deep blue solution with CuSO_4 solution
b. $(\text{NH}_4)_2\text{S}$	q. Produces deep blue ppt. with FeSO_4 solution
c. NH_4OH (excess)	r. Produces deep blue ppt. with FeCl_3 solution
d. NaOH (excess)	s. Produces colourless solution or white ppt. with ZnSO_4 solution
	t. Produces chocolate brown ppt. with CuSO_4 solution.

6. Match the substances given in column II based on reactions given in column I and select correct answer from the alternate:

Column I	Column II
a. A white, waxy solid, normally stored under water because it spontaneously inflames in air	p. HNO_3
b. A viscous liquid that reacts with BaCl_2 , giving a white ppt.	q. Cl_2
c. An acid that reacts with copper metal, releasing brown fumes	r. P
d. A pale greenish yellow gas that dissolves in aqueous NaOH to give a solution used as a bleach	s. H_2SO_4

7. Match the salts listed in column (I) with the colour of the precipitate and reagent(s) listed in column (II):

Column I		Column II	
a.	FeSO ₄	p.	Brown precipitate with NaOH
b.	Bi(NO ₃) ₃	q.	White precipitate with Pb(NO ₃) ₂
c.	AgNO ₃	r.	Yellow precipitate with NH ₄ NO ₂ and CH ₃ COOH on warming
d.	CoCl ₂	s.	Black precipitate with H ₂ S

8. Match the column:

Column I		Column II	
a.	$3\text{Fe}^{3+} + 6\text{CH}_3\text{COO}^\ominus \xrightarrow{\text{Boil}}$	p.	White ppt.
b.	$\text{S}_2\text{O}_3^{2-} + [\text{Ni}(\text{en})_3](\text{NO}_3)_2 \rightarrow$	q.	Blood-red colour
c.	$\text{Fe}^{3+} + \text{SCN}^\ominus \rightarrow$	r.	Violet ppt.
d.	$\text{CH}_3\text{COO}^\ominus + \text{AgNO}_3 \rightarrow$	s.	Brownish red ppt.

9. Match the column:

Column I		Column II	
a.	$\text{NH}_3 + \text{NaOCl} \xrightarrow{\Delta}$	p.	N ₂ O
b.	$\text{NH}_4\text{NO}_2 + \text{NaOH} \rightarrow$	q.	N ₂
c.	$\text{NH}_4\text{NO}_3 \xrightarrow{\Delta}$	r.	NH ₃
d.	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta}$	s.	H ₂ O

10. Match the column:

Column I		Column II	
a.	PbO ₂	p.	Soluble in excess alkali solution
b.	ZnO	q.	Form blue colour hydroxide with alkali solution
c.	HgCl ₂	r.	Reacts with NaOH to form coloured ppt.
d.	CuSO ₄	s.	Yellow on heating

11. There are certain chemical reagents which are used in the qualitative analysis of specific acid, i.e. anionic radicals. Match the reagent listed in column I with acid radicals listed in column II.

Column I		Column II	
a.	Silver nitrate solution	p.	CO ₃ ²⁻
b.	Barium chloride solution	q.	SO ₃ ²⁻
c.	Lead nitrate solution	r.	S ²⁻
d.	Acidified potassium permanganate solution	s.	NO ₂ [⊖]

12. Match the precipitates of the compounds listed in column I with the solvent(s) listed in column II:

Column I		Column II	
a.	Zn(OH) ₂ precipitate dissolves in	p.	Potassium cyanide
b.	Cr(OH) ₃ precipitate dissolves in	q.	Ammonia solution
c.	AgCl precipitate dissolves in	r.	Sodium hydroxide
d.	CuS precipitate dissolves in	s.	Sodium peroxide

13. Column (I) contains some reagents which when taken in excess produce precipitate with radical(s) given in column (II). Accordingly match column (I) with column (II):

Column I (Reagent)		Column II (Radical)	
a.	KCN _(aq)	p.	Pb ²⁺
b.	NaOH _(aq)	q.	Ag [⊕]
c.	KI _(aq)	r.	Hg ₂ ²⁺
d.	K ₂ CrO _{4(aq)}	s.	Cu ²⁺

14. Match the reactions listed in column (I) with the colour of the precipitate(s) listed in column (II):

Column I		Column II	
a.	$\text{Cu}^{2+}_{(aq)} + 2\text{SCN}^\ominus_{(aq)} \xrightarrow{\text{Allow to stand for sometime}}$	p.	Brown
b.	$\text{Pb}^{2+} + \text{CrO}_4^{2-} \rightarrow$	q.	Reddish brown ppt.
c.	$\text{CO}_3^{2-} + 4\text{Hg}^{2+} + 3\text{H}_2\text{O} \rightarrow$	r.	Yellow
d.	$\text{Mn}^{2+}_{(aq)} + 2\text{OH}^\ominus_{(aq)} \rightarrow$	s.	White

15. Match the column:

Column I		Column II	
a.	Red vapours	p.	MnSO ₄ + NaBiO ₃ + conc. HNO ₃
b.	NaOH solution is turned yellow by the vapours	q.	CrO ₂ Cl ₂
c.	Purple solution	r.	KBr heated with MnO ₂ and conc. H ₂ SO ₄
d.	A colourless solution results when the evolved gas is absorbed in an NaOH solution	s.	[Fe(CN) ₅ NOS] ⁴⁻

16. Match the column:

Column I		Column II	
a.	Blue, soluble in amyl alcohol	p.	$(\text{NH}_4)_2[\text{Co}(\text{SCN})_4]$
b.	White	q.	ZnS
c.	Obtained in the analysis of group III B	r.	PbSO_4
d.	Soluble in an ammonium acetate solution	s.	CrO_5

17. Certain substances change their colour when they are hot and revert to their original colour in cold. Match the following:

Column I		Column II	
a.	Yellow when hot and white in cold again	p.	Bi_2O_3 and SnO_2
b.	Yellowish brown in hot and yellow in cold	q.	ZnO
c.	Black or red in hot and brown in cold	r.	PbO
d.	Yellow in hot and yellow in cold	s.	Fe(III) oxide (Fe_2O_3)

18. Sometimes the original mixture gives characteristic smell. This also serves as an information in analysing the inorganic mixture. Match the following observation.

Column I		Column II	
a.	Vinegar or acetic acid type	p.	Ammonium salts, type $(\text{NH}_4)_2\text{CO}_3$
b.	Ammonical smell	q.	Acetates
c.	Chlorine gas smell	r.	Cyanides
d.	Bitter almond type smell	s.	Hypochlorites

19. Match the following flame tests:

Column I		Column II	
a.	Bright golden yellow	p.	Na
b.	Pale violet	q.	K
c.	Deep bluish green	r.	Cu
d.	Brick red	s.	Ca
e.	Crimson red	t.	Sr
f.	Pale green	u.	Ba

20. In borax bead test, the sodium metaborate (NaBO_2) and boric anhydride (B_2O_3) present in borax react with metallic salt to form coloured metaborates. The same metal can give different coloured beads in oxidising and reducing flames, due to formation of higher metaborates in oxidising flame and lower metaborates in reducing flame. Match the following:

Colour of bead in oxidising flame		Inference	
a.	Greenish when hot, blue in cold	p.	Cu
b.	Dark green in hot and cold	q.	Cr

c.	Deep blue	r.	Co
d.	Yellow when hot*	s.	Fe
e.	Violet in both hot and cold	t.	Mn
f.	Brown in cold	u.	Ni

21. In charcoal cavity test, the compound is mixed with Na_2CO_3 or with fusion mixture ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$) and placed in charcoal cavity, moistened with water and heated strongly. Match the following:

Metals		Bead and Incrustation	
a.	Bi	p.	Brittle beads, yellow
b.	Pb	q.	Soft beads, yellow which marks the paper
c.	Sb	r.	Brittle bead, white

22. The principle and procedure of cobalt nitrate test (or Rinmann's test) is exactly similar to that of charcoal cavity test with slight addition i.e. after adding Na_2CO_3 and heating, add few drops of cobalt nitrate and heat strongly. Match the following:

Observation		Composition		Inference	
a.	Blue residue	I.	$\text{CoO} \cdot \text{Al}_2\text{O}_3$	p.	Al (when phosphate and borate are absent)
b.	Green residue	II.	$\text{CoO} \cdot \text{ZnO}$	q.	ZnO
c.	Pink	III.	$\text{CoO} \cdot \text{MgO}$	r.	MgO
d.	Blue residue	IV.	NaCo PO_4	s.	Phosphate in absence of Al

23. Match the following using three columns with (X) containing radicals, (Y) the reagents used and (Z) the compound formed when (X) and (Y) react.

X		Y		Z	
a.	Fe^{2+}	I.	NH_4SCN	p.	Cherry red ppt.
b.	Fe^{3+}	II.	DMG	q.	Turnbull's blue
c.	Ni^{2+}	III.	$\text{K}_4[\text{Fe}(\text{CN})_6]$	r.	Prussian blue
d.	Co^{2+}	IV.	$\text{K}_3[\text{Fe}(\text{CN})_6]$	s.	Blue

24. Match the items given in Column I with that in Column II and III.

Column I		Column II		Column III	
Reaction of ions with reagent		Compound		Colour	
a.	Fe^{+2} with $[\text{Fe}(\text{CN})_6]^{4-}$	i.	$\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$	p.	White ppt
b.	Fe^{+2} with $[\text{Fe}(\text{CN})_6]^{3-}$	ii.	$\text{Fe}_2[\text{Fe}(\text{CN})_6]^{4-}$	q.	Prussian blue
c.	Fe^{+3} with $[\text{Fe}(\text{CN})_6]^{4-}$	iii.	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	r.	Brown solution
d.	Fe^{+3} with $[\text{Fe}(\text{CN})_6]^{3-}$	iv.	$\text{Fe}[\text{Fe}(\text{CN})_6]^{3-}$	s.	Turnbull's blue

25. Match the items given in Column I with that in Column II and III.

Column I		Column II		Column III	
Ions		Reagent		Colour	
a.	Zn^{+2}	i.	$[\text{Fe}(\text{CN})_6]^{3-}$	p.	Blue colour
b.	Co^{+2}	ii.	SCN^-	q.	Reddish brown ppt

c.	Cu^{+2}	iii.	$[\text{Fe}(\text{CN})_6]^{4-}$	r.	Chocolate colour ppt
d.	Fe^{+3}	iv.	8-Hydroxy-quinoline	s.	Bluish white colour
e.	Al^{+3}	v.	1, 10-Phenanthroline		Blood red colour

26. Match the items given in Column I with that in Column II and III.

Column I		Column II		Column III	
Separation		Reagent		Inference	
a.	Mixture of Co^{+2} and Ni^{2+} are distinguished by	i.	Addition of KCN	p.	Gives ppt soluble in NH_4OH and another ppt insoluble in NH_4OH
b.	Mixture of Br^- and I^- are distinguished by	ii.	Addition of $[\text{Fe}(\text{CN})_6]^{4-}$	q.	Forms complexes and on passing $\text{H}_2\text{S}(\text{g})$. Unstable complex gives yellow ppt
c.	Mixture of Cu^{2+} and Cd^{2+} are distinguished by	iii.	Layer test	r.	Gives red colour with one ions and no colour with other ion
d.	Mixture of SO_3^{2-} and SO_4^{2-} are distinguished by	iv.	FeCl_3 solution	s.	First turns violet and then brown on excess of addition of Cl_2

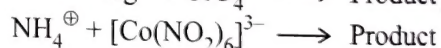
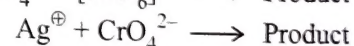
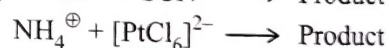
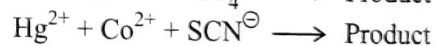
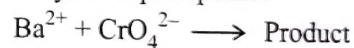
Numerical Value Type

- An aqueous solution contains Hg^{2+} , Hg_2^{2+} , Pb^{2+} and Cd^{2+} . Out of these, how many ions will produce white precipitate with dilute HCl?
- How many compounds liberate NH_3 on heating from the following:
 $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{CO}_3$, NH_4Cl , NH_4NO_3 , $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
- How many water molecule(s) is/are present in microcosmic salt?
- Na_2SO_3 , NaCl , $\text{Na}_2\text{C}_2\text{O}_4$, Na_2HPO_4 , Na_2CrO_4 , NaNO_2 , $\text{CH}_3\text{CO}_2\text{Na}$ are separately treated with AgNO_3 solution. In how many cases is/are white ppt. obtained?
- Find the number of compounds which have yellow colour ppt. from the given compounds:
 Ag_2CrO_4 , PbCrO_4 , Hg_2CrO_4 , BaCrO_4
- Find the number of ions which are identified by dil. HCl from the following:
(i) CO_3^{2-} (ii) SO_3^{2-} (iii) SO_4^{2-}
- Find the number of reducing agents from the following:
 H_2S , SO_3 , CrO_4^{2-} , Fe^{2+} , MnO_4^-
- How many water of crystallisation is(are) present in the ore carnallite?
- $\text{BO}_3^{3-} + \text{conc. H}_2\text{SO}_4 + \text{CH}_3 - \text{CH}_2 - \text{OH} \xrightarrow{\text{ignite}} (\text{A})$

Green flame

What is the oxidation number of central atom that is responsible for green flame in compound (A)?

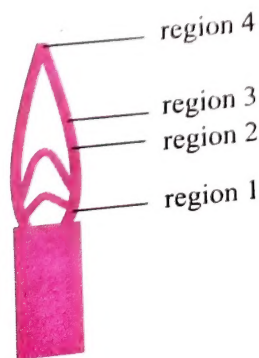
- Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$, Na_2CO_3 , Na_2CrO_4 are separately treated with AgNO_3 solution. In how many cases is/are red ppt. obtained?
- In how many of the following reactions, one of the products is obtained as a yellow precipitate?



- A solution of Hg^{2+} ion on treatment with a solution of cobalt(II) thiocyanate gives rise to a deep blue crystalline precipitate. Then the coordination number of mercury in the deep blue coloured compound is.
- How many water molecule(s) is/are present in compound which is used in borax bead test?
- $\text{Fe}^{2+}_{(\text{aq})} + \text{NO}_3^-_{(\text{aq})} + \text{H}_2\text{SO}_4(\text{conc.}) \longrightarrow \text{Brown ring}$
The oxidation number of iron in brown ring complex is.
- In how many of the following reactions one of the products is obtained as a black precipitate?
 - $\text{Bi}(\text{OH})_3 \downarrow + [\text{Sn}(\text{OH})_4]^{2-}_{(\text{aq})} \longrightarrow \text{Products}$
 - $\text{Bi}^{3+}_{(\text{aq})} + \text{I}^-_{(\text{aq})} (\text{not in excess}) \longrightarrow \text{Products}$
 - $\text{Ag}^+_{(\text{aq})} + \text{H}_2\text{S}_{(\text{g})} \xrightarrow{\text{H}^+} \text{Products}$
 - $[\text{BiI}_4]^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \xrightarrow{\text{Dilution}} \text{Products}$

Single Correct Answer Type

- $[X] + H_2SO_4 \longrightarrow [Y]$ a colorless gas with irritating smell, $[Y] + K_2Cr_2O_7 + H_2SO_4 \rightarrow$ Green solution, $[X]$ and $[Y]$ are
 (1) SO_3^{2-} and SO_2 (2) Cl^- and HCl
 (3) S^{2-} and H_2S (4) CO_3^{2-} and CO_2
(AIEEE 2010)
- A salt of $NaX \xrightarrow{MgCl_2}$ White ppt. on boiling. Thus, anion X is
 (1) HCO_3^- (2) NO_3^-
 (3) CO_3^{2-} (4) SO_4^{2-}
(AIEEE 2010)
- Passing H_2S gas into a mixture of Mn^{2+} , Ni^{2+} , Cu^{2+} , and Hg^{2+} ions in an acidified aqueous solution precipitates
 (1) CuS and HgS (2) MnS and CuS
 (3) MnS and NiS (4) NiS and HgS
(AIEEE 2011)
- The color of light absorbed by an aqueous solution of $CuSO_4$ is
 (1) Orange-red (2) Blue-green
 (3) Yellow (4) Violet
(AIEEE 2011)
- In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are
 (1) O_2 and CO , respectively
 (2) O_2 and Zn dust, respectively
 (3) HNO_3 and Zn dust, respectively
 (4) HNO_3 and CO , respectively
(AIEEE 2012)
- The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was
 (1) Ammonia (2) Phosgene
 (3) Methylisocyanate (4) Methylamine
(JEE Main 2013)
- Which of the following is the wrong statement?
 (1) Ozone is violet-black in solid state.
 (2) Ozone is diamagnetic gas.
 (3) $ONCl$ and ONO^- are isoelectronic
 (4) O_3 molecule is bent.
(JEE Main 2013)
- The hottest region of Bunsen flame shown in the figure below is:



- (1) region 4 (2) region 1
 (3) region 2 (4) region 3

(JEE Main 2016)

- Sodium salt of an organic acid ' X ' produces effervescence with conc. H_2SO_4 . ' X ' reacts with the acidified aqueous $CaCl_2$ solution to give a white precipitate which decolourises acidic solution of $KMnO_4$. ' X ' is:
 (1) C_6H_5COONa (2) $HCOONa$
 (3) CH_3COONa (4) $Na_2C_2O_4$
(JEE Main 2017)

- An alkali is titrated against an acid with methyl orange as indicator. Which of the following is a correct combination?

	Base	Acid	End point
(1)	Strong	Strong	Pinkish red to yellow
(2)	Weak	Strong	Yellow to pinkish red
(3)	Strong	Strong	Pink to colourless
(4)	Weak	Strong	Colourless to pink

(JEE Main 2018)

JEE ADVANCED

Single Correct Answer Type

- Sulphide ores are common for the metals
 (1) Ag , Cu and Pb (2) Ag , Cu and Ni
 (3) Ag , Mg and Pb (4) Al , Cu and Pb
(JEE Advanced 2013)
- Upon treatment with ammoniacal H_2S the metal ion that precipitates as sulphide is
 (1) $Fe(III)$ (2) $Al(III)$
 (3) $Mg(II)$ (4) $Zn(II)$
(JEE Advanced 2013)
- Roasting of sulphides gives the gas X as a by product. This is a colourless gas with choking smell of burnt sulphur and causes great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic, acts as a reducing agent and its acid has never been isolated. The gas X is
 (1) CO_2 (2) SO_3
 (3) H_2S (4) SO_2
(JEE Advanced 2013)
- Identify the correct order of solubility in aqueous medium:
 (1) $Na_2S > CuS > ZnS$ (2) $Na_2S > ZnS > CuS$
 (3) $CuS > ZnS > Na_2S$ (4) $ZnS > Na_2S > CuS$
(JEE Advanced 2013)
- Which of the following compounds is not colored yellow?
 (1) $Zn_2[Fe(CN)_6]$ (2) $K_3[Co(NO_2)_6]$
 (3) $(NH_4)_3[As(MO_3O_{10})_4]$ (4) $BaCrO_4$
(JEE Advanced 2015)

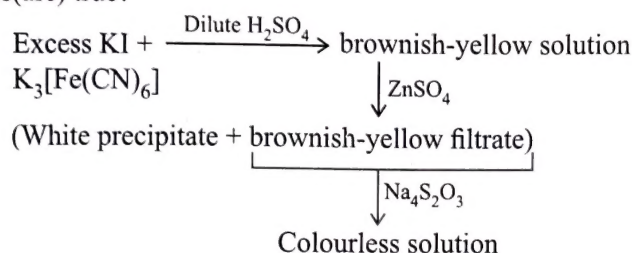
Multiple Correct Answers Type

1. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is/are

- (1) NH_4NO_3 (2) NH_4NO_2
(3) NH_4Cl (4) $(\text{NH}_4)_2\text{SO}_4$

(IIT-JEE 2008)

2. For the given aqueous reaction, which of the statement(s) is/are true?



- (1) The first reaction is a redox reaction.
(2) White precipitate is $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$.
(3) Addition of filtrate to starch solution gives blue colour.
(4) White precipitate is soluble in NaOH solution.

(IIT-JEE 2012)

3. The pair(s) of ions where BOTH the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is/are)

- (1) Ba^{2+} , Zn^{2+} (2) Bi^{3+} , Fe^{3+}
(3) Cu^{2+} , Pb^{2+} (4) Hg^{2+} , Bi^{3+}

(JEE Advanced 2015)

4. The reagent(s) that can selectively precipitate S^{2-} from a mixture of S^{2-} and SO_4^{2-} in aqueous solution is (are)

- (1) CuCl_2 (2) BaCl_2
(3) $\text{Pb}(\text{OOCCH}_3)$ (4) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$

(JEE Advanced 2016)

Linked Comprehension Type

Paragraph 1

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (P) and a filtrate (Q). The precipitate P was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with H_2S in a dilute mineral acid medium. However, it gave a precipitate (R) with H_2S in an ammoniacal medium. The precipitate R gave a coloured solution (S), when treated with H_2O_2 in an aqueous NaOH medium.

1. The precipitate P contains

- (1) Pb^{2+} (2) Hg_2^{2+}
(3) Ag^+ (4) Hg^{2+}

2. The coloured solution S contains

- (1) $\text{Fe}_2(\text{SO}_4)_3$ (2) CuSO_4
(3) ZnSO_4 (4) Na_2CrO_4

(JEE Advanced 2013)

Numerical Value Type

1. Among PbS , CuS , HgS , MnS , Ag_2S , NiS , CoS , Bi_2S_3 and SnS_2 , the total number of BLACK coloured sulphides is

(JEE Advanced 2014)

Answers Key

EXERCISES

Single Correct Answer Type

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (2) | 2. (2) | 3. (3) | 4. (4) | 5. (2) |
| 6. (1) | 7. (1) | 8. (1) | 9. (1) | 10. (3) |
| 11. (1) | 12. (1) | 13. (3) | 14. (2) | 15. (4) |
| 16. (2) | 17. (2) | 18. (2) | 19. (2) | 20. (4) |
| 21. (2) | 22. (4) | 23. (1) | 24. (3) | 25. (3) |
| 26. (2) | 27. (2) | 28. (4) | 29. (4) | 30. (1) |
| 31. (3) | 32. (3) | 33. (4) | 34. (4) | 35. (3) |
| 36. (1) | 37. (2) | 38. (4) | 39. (3) | 40. (2) |
| 41. (4) | 42. (4) | 43. (2) | 44. (1) | 45. (1) |
| 46. (1) | 47. (4) | 48. (1) | 49. (3) | 50. (3) |
| 51. (2) | 52. (2) | 53. (1) | 54. (3) | 55. (1) |
| 56. (4) | 57. (2) | 58. (2) | 59. (3) | 60. (4) |
| 61. (1) | 62. (1) | 63. (1) | 64. (2) | 65. (4) |
| 66. (3) | 67. (4) | 68. (2) | 69. (4) | 70. (2) |
| 71. (2) | 72. (1) | 73. (3) | 74. (2) | 75. (4) |

- | | | | | |
|----------|----------|----------|----------|----------|
| 76. (3) | 77. (3) | 78. (2) | 79. (3) | 80. (2) |
| 81. (3) | 82. (3) | 83. (3) | 84. (4) | 85. (1) |
| 86. (3) | 87. (3) | 88. (3) | 89. (1) | 90. (4) |
| 91. (4) | 92. (3) | 93. (4) | 94. (3) | 95. (1) |
| 96. (3) | 97. (3) | 98. (4) | 99. (3) | 100. (4) |
| 101. (3) | 102. (3) | 103. (1) | 104. (1) | 105. (4) |
| 106. (4) | 107. (4) | 108. (1) | 109. (2) | 110. (1) |
| 111. (3) | 112. (3) | 113. (1) | 114. (2) | 115. (2) |
| 116. (2) | 117. (2) | 118. (4) | 119. (1) | 120. (1) |
| 121. (4) | 122. (1) | 123. (1) | 124. (4) | 125. (4) |
| 126. (1) | 127. (4) | 128. (4) | 129. (2) | 130. (3) |
| 131. (2) | 132. (1) | 133. (2) | 134. (3) | 135. (2) |
| 136. (1) | 137. (2) | 138. (1) | 139. (3) | 140. (4) |
| 141. (3) | 142. (1) | 143. (4) | 144. (1) | 145. (4) |
| 146. (2) | 147. (2) | 148. (2) | 149. (3) | 150. (1) |
| 151. (2) | 152. (1) | 153. (1) | 154. (1) | 155. (2) |
| 156. (3) | 157. (4) | 158. (4) | 159. (3) | 160. (1) |
| 161. (1) | 162. (3) | | | |

Multiple Correct Answers Type

1. (1, 2) 2. (1, 3, 4) 3. (1, 2, 3)
 4. (2, 3, 4) 5. (2, 3) 6. (3, 4)
 7. (1, 2, 3) 8. (3, 4) 9. (1, 2, 3)
 10. (1, 2, 4) 11. (1, 2, 3) 12. (1, 2, 3)
 13. (1, 2, 3) 14. (1, 2, 4) 15. (1, 2, 3)
 16. (1, 2) 17. (1, 3, 4) 18. (1, 2, 3, 4)
 19. (1, 2, 3, 4) 20. (1, 2) 21. (1, 2, 4)
 22. (2, 3, 4) 23. (2, 3) 24. (1, 2)
 25. (1, 2, 3, 4) 26. (2, 3, 4) 27. (3, 4)
 28. (1, 2, 4) 29. (1, 3) 30. (1, 3, 4)
 31. (1, 2, 3) 32. (1, 2) 33. (1, 2, 3)
 34. (3, 4) 35. (1, 2) 36. (2, 4)
 37. (3, 4) 38. (1, 3, 4) 39. (1, 3, 4)
 40. (1, 2, 4) 41. (1, 2, 3) 42. (1, 2, 3)
 43. (1, 3) 44. (1, 2, 3) 45. (2, 3, 4)
 46. (2, 3, 4) 47. (1, 2) 48. (3, 4)
 49. (1, 2, 3) 50. (1, 2, 3) 51. (1, 2)
 52. (1, 2) 53. (2, 3) 54. (1, 3)
 55. (2, 3) 56. (1, 3, 4) 57. (1, 2, 3, 4)
 58. (1, 3, 4) 59. (1, 2, 3) 60. (1, 2, 3)
 61. (1, 4) 62. (1, 3) 63. (3, 4)
 64. (1, 2, 3) 65. (1, 3, 4) 66. (1, 4)
 67. (1, 3) 68. (1, 3, 4) 69. (1, 2)
 70. (1, 2, 3, 4) 71. (2, 3) 72. (1, 3, 4)
 73. (1, 2) 74. (1, 3, 4) 75. (1, 2, 3, 4)
 76. (1, 2, 3) 77. (2, 3) 78. (1, 3)
 79. (1, 2, 3, 4) 80. (1, 2, 3, 4) 81. (1, 2, 3)
 82. (2, 3, 4) 83. (1, 2, 3) 84. (1, 2, 3, 4)
 85. (1, 3, 4) 86. (1, 2, 4) 87. (1, 2, 4)
 88. (1, 2, 3, 4) 89. (1, 2)

4.	q	r	s	s	p	—
5.	r, s, t	s	p, s	s	—	—
6.	r	s	p	q	—	—
7.	p, q, s	s	p, s	r, s	—	—
8.	s	r	q	p	—	—
9.	q, s	r, s	p, s	q, s	—	—
10.	p	p, s	r	q, r	—	—
11.	p, q, r, s	p, q	p, q, r	q, r, s	—	—
12.	p, q, r	q, r, s	p, q	p, s	—	—
13.	p, r	q, r, s	q, r, s	p, q, r	—	—
14.	s	r	q	p	—	—
15.	q, r	p	p, s	r	—	—
16.	p, s	q, r	p, q	r	—	—
17.	q	p	s	r	—	—
18.	q	p	s	r	—	—
19.	p	q	r	s	t	u
20.	p	q	r	s	t	u
21.	p	q	r		—	—
22.	I-p	II-q	III-r	IV-s	—	—
23.	IV-q	III-r	II-p	I-s	—	—
24.	ii-p	i-s	iii-q	iv-r	—	
25.	iii-s	i, ii-p, q	iii-r	ii, v-t, q	iv-p	
26.	ii-p	iii-s	i-q	iv-r		

Numerical Value Type

1. (2) 2. (3) 3. (4) 4. (5) 5. (2)
 6. (2) 7. (2) 8. (6) 9. (3) 10. (1)
 11. (3) 12. (4) 13. (10) 14. (1) 15. (3)

ARCHIVES

JEE Main

Single Correct Answer Type

1. (1) 2. (1) 3. (1) 4. (1) 5. (2)
 6. (3) 7. (3) 8. (3) 9. (4) 10. (2)

JEE Advanced

Single Correct Answer Type

1. (1) 2. (4) 3. (4) 4. (2) 5. (1)

Multiple Correct Answers Type

1. (1, 2) 2. (1, 3, 4) 3. (3, 4) 4. (1, 3)

Linked Comprehension Type

1. (1) 2. (4)

Numerical Value Type

1. (7)

Linked Comprehension Type

1. (3) 2. (1) 3. (2) 4. (2) 5. (3)
 6. (2) 7. (1) 8. (2) 9. (3) 10. (1)
 11. (2) 12. (2) 13. (1) 14. (4) 15. (3)
 16. (4) 17. (1) 18. (3) 19. (3) 20. (2)
 21. (2) 22. (2) 23. (2) 24. (2) 25. (2)
 26. (2) 27. (1) 28. (1) 29. (2) 30. (3)
 31. (1) 32. (2) 33. (3) 34. (2) 35. (2)
 36. (3) 37. (3) 38. (2) 39. (1) 40. (3)
 41. (2) 42. (3) 43. (3) 44. (2) 45. (1)
 46. (3) 47. (2) 48. (2) 49. (4) 50. (1)
 51. (1) 52. (3) 53. (2) 54. (2) 55. (2)
 56. (4) 57. (1, 2) 58. (1, 2) 59. (1, 3) 60. (2)
 61. (2) 62. (2) 63. (3) 64. (3) 65. (1)
 66. (2) 67. (3) 68. (1)

Matrix Match Type

Q.No.	a.	b.	c.	d.	e.	f.
1.	s	q	p	p	r	—
2.	p, r	p	p, s	q, s	—	—
3.	q	r	p	s	—	—